SUMMARY OF TECHNOLOGIES FOR THE CONTROL AND REDUCTION OF CHLORINATED ORGANICS FROM THE BLEACHED CHEMICAL PULPING SUBCATEGORIES OF THE PULP AND PAPER INDUSTRY

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Water Regulations and Standards
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401 M Street S.W.
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GLOSSARY OF ACRONYMS AND ABBREVIATIONS

ADBSP	air dried brownstock pulp
ADMT	air dried metric tons
ADST	air dried short tons
AOX	adsorbable organic halogen
AQ	anthraquinone
ASB	aerated stabilization basin - A natural or man made wastewater treatment pond in which mechanical or diffused air is used to supplement the oxygen supply.
BAT	Best Available Technology Economically Achievable
BOD or BOD_5	biochemical oxygen demand (five day) - The amount of dissolved oxygen consumed in five days by biological processes breaking down organic matter under standard conditions.
BOD_7	biochemical oxygen demand (seven day) - The amount of dissolved oxygen consumed in seven days by biological processes breaking down organic matter under standard conditions.
C	chlorine - A bleaching stage where pulp is treated with gaseous chlorine, primarily to oxidize the residual lignin, so that it can later be dissolved and extracted with sodium hydroxide.
CAC	chemically assisted clarification
C/D	Sequential addition of chlorine and chlorine dioxide in the same bleaching stage.
CDD	chlorinated dibenzo-p-dioxin
CDF	chlorinated dibenzofuran
CDN$	Canadian dollars - As of 29 March 1990, 1 CDN$ = $0.850
CEK No.	caustic extraction K-number - A parameter monitored in bleaching operations after the chlorine stage which can be used to determine how much chlorine or chlorine dioxide to add.
COD	chemical oxygen demand - A measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant.
CTMP	chemi-thermomechanical pulp
D	chlorine dioxide - A bleaching stage where the pulp is treated with chlorine dioxide, applied in an aqueous solution.
DBF	unchlorinated dibenzofuran
DBD	unchlorinated dibenzo-p-dioxin
D/C	Sequential addition of chlorine dioxide and chlorine in the same bleaching stage. Implies greater than 20% chlorine substitution.
E	caustic extraction - A bleaching stage involving dissolution of reaction products with sodium hydroxide.
E_O	caustic extraction with oxygen enhancement - Also referred to as oxygen extraction.
EOCl	extractable organic chlorine
E_{OP}	peroxide reinforced oxygen extraction
EOX	extractable organic halogens
E_P	caustic extraction with peroxide enhancement
g/adt	grams per air dried metric ton
GE	Unit of brightness determined by use of a General Electric reflectance meter.
GJ	gigijoules = one billion joules
H	hypochlorite - A bleaching stage involving the treatment of pulp with sodium or calcium hypochlorite.
ISO	Unit of brightness (International Organization for Standardization). Uses different optical geometry and different reference standard than TAPPI or GE method. ISO brightness is slightly lower than GE brightness.
K No.	permanganate number
kg/ton	kilogram per metric ton
kwH	kilowatt hour
L	hypochlorous acid - A bleaching stage involving the treatment of pulp with hypochlorous acid.

LRP	Lignin Removal Process - A proprietary process for the precipitation of high molecular organic compounds.
m^3/adt	cubic meters per air dried metric ton
mg/l	milligrams per liter = ppm
MCC	Modified Continuous Cook - A proprietary process for extended delignification in a continuous digester.
MGD	million gallons per day
N	nitrogen dioxide - A bleaching stage where the pulp is treated with nitrogen dioxide.
ng/l	nanograms per liter = ppt
NCASI	National Council of the Paper Industry for Air and Stream Improvement, Inc.
ND	nondetect
NQ	not quantified
NTU	nephelometric turbidity units
O	oxygen - A bleaching stage where the pulp is treated with elemental oxygen, in alkaline conditions.
od	oven dry
OD	oxygen delignification
P	peroxide - A bleaching stage where the pulp is treated with hydrogen or sodium peroxide.
PAPRICAN	Pulp and Paper Research Institute of Canada
PCDD	polychlorinated dibenzo-p-dioxin - Includes all isomers of which there are 75.
PCDF	polychlorinated dibenzofuran - Includes all isomers of which there are 135.
PCU	platinum cobalt color units - A unit of measurement for color which also can be expressed as mg/l.
pg/l	picograms per liter = ppq
ppb	parts per billion (10^{-9})
ppm	parts per million (10^{-6})
ppq	parts per quadrillion (10^{-15})
ppt	parts per trillion (10^{-12})
RDH	Rapid Displacement Heating - A proprietary extended delignification process for batch digestion systems.
ROI	return on investment
SEK	Swedish kroner - As of 29 March 1990, 1 SEK = $0.162
SLC	Suppressed Lignin Condensation - A proprietary process designed to reduce the amount of dissolved lignin which precipitates back into the fibers after the chlorine stage of bleaching.
SNV	Statens Naturvårdsverk (Swedish National Environmental Protection Board)
STFI	Skogsindustrins Tekniska Forskningsinstitut (Swedish Pulp and Paper Research Institute)
s.u.	standard units
TAPPI	Technical Association of the Pulp and Paper Industry
TCDD	tetrachlorodibenzo-p-dioxin
TCDF	tetrachlorodibenzofuran
TMP	thermomechanical pulping
TOCl	total organic chlorine
tonne	metric ton
TOX	total organic halogen
µg/g	micrograms per gram = ppm(10^{-6})
Y	hydrosulphite - A bleaching stage where the pulp is treated with sodium or zinc hydrosulphite.
Z	ozone - A bleaching stage where the pulp is treated with ozone under acid conditions.

I. INTRODUCTION/BACKGROUND

The purpose of this report is to identify and describe technologies and/or processes under evaluation, development or in use with potential to reduce or eliminate the formation of chlorinated organics during the chlorine bleaching of chemically produced pulps. A manual literature search as well as a computerized literature search of the following data bases was performed: (1) PAPERCHEM, (2) NTIS, (3) CHEM ABSTRACTS, (4) DISSERTATION ABSTRACTS, AND (5) PAPRICAN. Applicable articles were obtained and a list of those articles the majority of which were used in developing this paper can be found in **Attachment A.**

The literature does not reveal any single process that can entirely eliminate chlorinated organics as well as maintain the final high brightness needed to produce quality market pulp and/or paper. These chlorinated organics are usually measured as Total Organic Chlorine (TOCl) or as Adsorbable Organic Halogen (AOX). Numerous studies have shown that the formation of chlorinated organics are reduced with reduced elemental chlorine (Cl_2) consumption.[17,19,22,92] The two main approaches described in the literature to decrease chlorine consumption are: (a) process modifications which reduce the amount of lignin in pulp entering the bleach plant, thus, minimizing bleaching chemical demand (e.g., oxygen delignification and extended delignification); and (b) process modifications which minimize the consumption of chlorine and chlorine bleaching products during bleaching (e.g., chlorine dioxide substitution and alkaline extraction in the presence of oxygen). **Figure I-1** shows how various process modifications can aid in reducing formation of TOCl.

Brief descriptions of each technology are provided in the following pages. In addition to a description of the technology, the relative effectiveness of the technology, installations, implementation and cost of the technologies identified, are discussed where information was available. The effectiveness of each technology was assessed on the basis of it's ability to reduce chlorinated organics or chlorine consumption. The section on installation lists facilities where the technology is presently in operation, under construction or planned. Implementation was assessed on the basis of the compatibility and/or impact on other processes, effects on pulp, availability, time to implement and limitations. The section on costs covers capital and operating costs where information was available. A list of recent literature references keyed to **Attachment A**, is also presented for each technology.

Those technologies that have been developed and studied on a mill-scale basis and are being applied in the industry have been included in this report under Available Technologies. Other technologies, including alternate pulping and bleaching technologies which have not been demonstrated on a commercial scale, are referred to as Emerging Technologies.

Those unfamiliar with the pulp and paper industry are advised to consult Reference's 92, 131 and 145 from which much of the introductory material in this report was abstracted, and Reference 138 which presents the results of the first comprehensive dioxin study of pulp and paper mills.

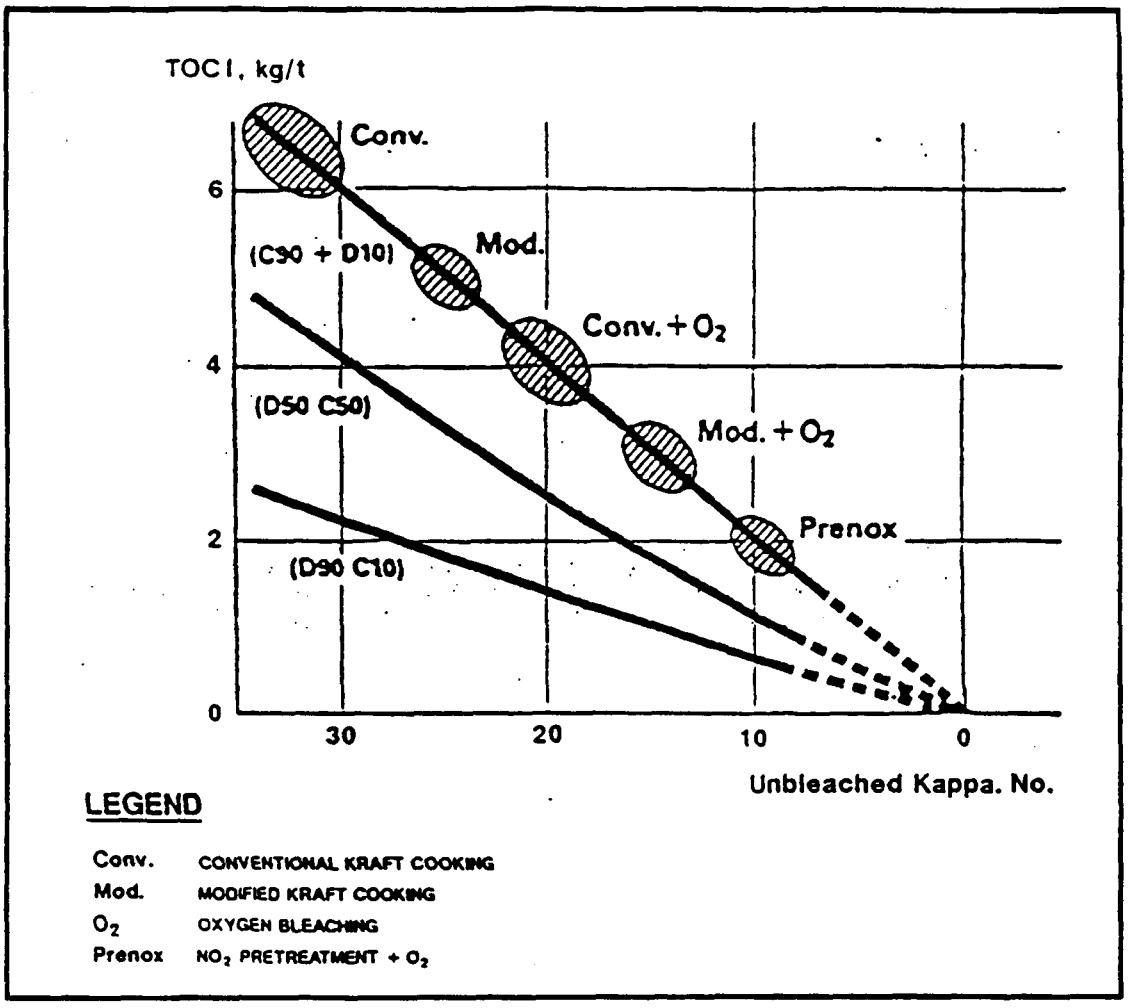

FIGURE I-1 EFFECT OF KAPPA NUMBER AND CHLORINE DIOXIDE SUBSTITUTION ON FORMATION OF TOCl[22]

II. CHLORINATED ORGANIC COMPOUNDS PRODUCED IN BLEACHED CHEMICAL PULP MILLS

WOOD COMPOSITION

The principal components of wood are cellulose, hemicelluloses, lignin, and extractives. Cellulose, a linear polysaccharide, is the characteristic wall material of plant cells. Cellulose molecules are bundled together in wood to form microfibrils, which in turn build up to form fibrils, and finally cellulose fibers. About 40% of most wood is cellulose.[92]

Hemicelluloses, also polysaccharides, are composed of different carbohydrate units. Unlike cellulose, hemicelluloses are branched to various degrees and their molecular masses are much lower. Hemicelluloses can also be distinguished analytically from cellulose by their greater ease of hydrolysis in hot dilute acid solutions, and their solubility in aqueous alkaline solutions. The content and types of hemicellulose in softwoods differ considerably from those in hardwoods.[92]

Lignin is an amorphous partly aromatic polymer. It imparts rigidity to the fiber walls and acts as a bonding agent between fibers. Lignin is partly soluble in aqueous alkaline solutions, condenses in mineral acids and is readily attacked and solubilized by oxidizing agents. The relative molecular mass of native lignin is considered infinite.[92]

"Extractives" are those low molecular components of wood that can be extracted with water or organic solvents such as ethanol, acetone, or dichloromethane and excludes those components defined as hemicellulose or lignin.[131] The amount of extractives in wood varies greatly (1.5-5%), depending upon species, place of growth, and age of the tree.[92] Extractives include aliphatics consisting of fats and waxes; phenolic extractives, which include hydrolyzable tannins, flavonoids, ligands, stilbenes, and tropolines; and, terpenoid compounds found only in softwoods, which include mono-, sesqui-, and diterpenes, as well as various resin acids.[92]

CHEMICAL WOOD PULPING

Most chemical pulping in the United States is currently carried out by the kraft (sulfate) or the sulfite process. The purposes of pulping are to remove lignin in order to facilitate fiber separation and to improve the papermaking properties of the fibers. The kraft process is the most widely used commercial process, by far. In the United States, there are 87 bleached kraft mills and 17 bleached sulfite mills.[126] Kraft pulping entails treating wood chips at 160-180° C with a liquor containing sodium hydroxide and sodium sulfide, which promotes cleavage of the various ether bonds in the lignin. The lignin degradation products so formed dissolve in the alkaline pulping liquor. Depending upon pulping conditions, as much as 90-95% of the lignin can be removed from wood in kraft pulping.[92]

Portions of the wood polysaccharides, especially those associated with the hemicelluloses, and most of the wood extractives are dissolved in the kraft pulping liquor. If softwood is the raw material, the extractives can be recovered as by-products such as sulfate turpentine and tall oil. Turpentine contains a mixture of the lower terpenes, whereas

raw tail oil consists mainly of fatty and resin acids. The content of residual extractives in unbleached (brownstock) pulp is low.[92]

In kraft pulping for production of bleached pulp, more than 55% of the total weight of wood is dissolved in the pulping liquor. After separation from the pulp, the spent liquor is evaporated to a high concentration and then burned in a recovery boiler to recover energy and inorganic chemicals which are used to re-constitute fresh pulping liquor.[92]

By comparison, the sulfite process solubilizes lignin through sulfonation at elevated temperatures. The pulping liquor contains sulfur dioxide and alkaline oxides (sodium, magnesium, or calcium).[92] With the exception of sulfite mills using a calcium based cooking liquor, the cooking liquor is evaporated and burned in a recovery boiler to recover energy and inorganic chemicals which are used to make up new cooking liquor.

The lignin content of unbleached or brownstock pulps is characterized by the kappa number, or the permanganate (K) number. Kappa numbers for unbleached softwood kraft pulps are generally in the range of 28 to 35, while those for hardwood kraft pulps may range from 14 to 18. For softwood pulps, permanganate numbers are about one third lower than corresponding kappa numbers, and, for hardwood pulps about 30% lower.

PULP BLEACHING

As noted above, not all of the lignin is removed from wood during chemical pulping. About five to ten% of the original lignin remains in the pulp since it cannot be removed by extended conventional pulping without degrading the polysaccharide fraction. Removal of the residual lignin that is responsible for the dark color of kraft pulps, requires a multistage bleaching process.[92] **Figure II-1** illustrates conventional kraft pulping and bleaching processes for producing bleached softwood pulps. In virtually all kraft mills, bleaching is accomplished by successive treatments of the kraft pulps in slurry form with chlorine (C) and alkali extraction (E) (sodium hydroxide), followed by other bleaching stages which may include chlorine dioxide (D), sodium or calcium hypochlorite (H), and hydrogen peroxide (P). A list of the symbols used to denote bleaching stages is shown in **Table II-1.**

The first C and E-stages of a normal bleach sequence constitute prebleaching and all subsequent stages collectively are referred to as final bleaching. Additional extraction stages are usually included in long sequence bleach lines. After each bleaching or extraction stage, the pulp is washed using either fresh water or recirculated water from other bleachery washing stages of similar pH. Excess water discharged from the washers constitute the bleachery effluent.

The largest quantity of unwanted material is dissolved from the pulp in the prebleaching C and E-stages. It is from these two stages that the vast majority of dioxins and furans as well as other chlorinated organics are discharged. The C-stage consists of treatment of the pulp slurry with elemental chlorine, or combinations of chlorine dioxide and elemental chlorine . The slurry consistency is normally in the range of three% and, depending upon the lignin content of the brownstock pulp, the chlorine charge may range from 70 to more than 200 lbs/ton for softwood pulps and from 25 to more than 100 lbs/ton for hardwood pulps. The temperature in the C-stage is usually 15 to 30° C,

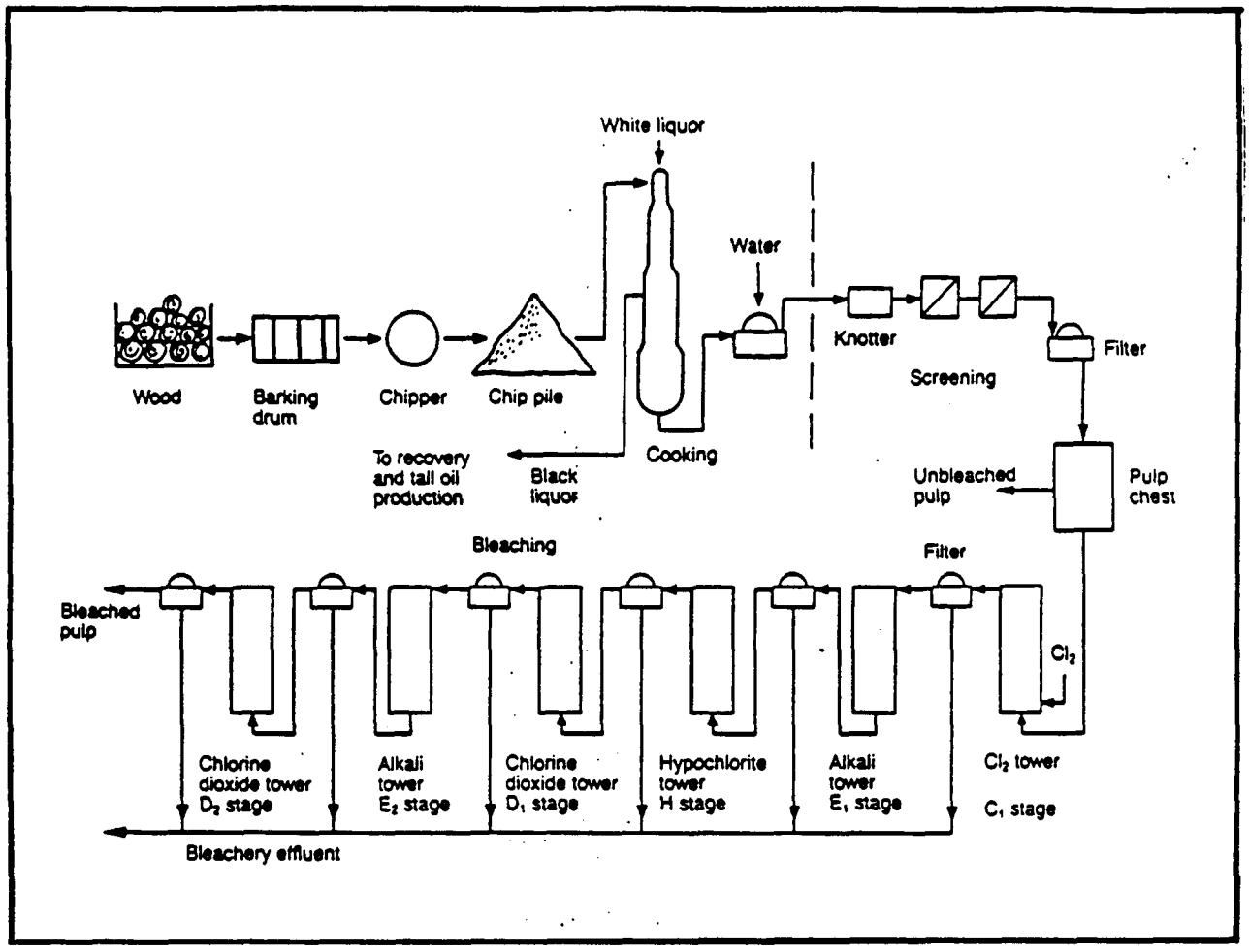

FIGURE II-1 KRAFT PULP MILL, INCLUDING A CONVENTIONAL BLEACH PLANT[131]

and the final pH is in the range of 1.5 to 2.0 s.u..[92,126] The amount of chlorine and chlorine dioxide required in prebleaching is directly related to the lignin content of the incoming pulp.

TABLE II-1

BLEACHING SYMBOLS

SYMBOL	
C	chlorine [Cl_2]
D	chlorine dioxide [ClO_2]
E	alkaline extraction [NaOH]
H	hypochlorite [NaOCl or $Ca(OCl)_2$]
L	hypochlorous acid [HClO]
O	oxygen [O_2]
N	nitrogen dioxide [NO_2]
P	peroxide [H_2O_2 or Na_2O_2]
Y	hydrosulphite [$Na_2S_2O_4$ or ZnS_2O_4)
Z	ozone [O_3]

The E stage is an extraction of the chlorinated pulp with alkali, usually sodium hydroxide. More recent practice is to add oxygen to the E-stage to enhance lignin removal thus reducing the amount of bleach chemical needed in subsequent stages. The consistency in the E-stage is usually raised to more than 10% by removing water from the chlorinated pulp prior to extraction. The reaction temperature is raised to 55 to 70° C and the final pH is about 11 s.u..[92] In subsequent final bleaching stages, less aggressive treatments are used to achieve desired final pulp brightness required for specific end uses.

During conventional bleaching of softwood kraft pulp, about 170 lbs/ton of material is dissolved into bleaching liquors. About 120 lbs/ton originates from the residual lignin; about 46 lbs/ton comes from the polysaccharide fraction; and about 5 lbs/ton is from the extractives portion of the pulp.[92] About 75% of this material is dissolved during the C and E stages.[92]

In pulp chlorination, chlorine reacts primarily with residual lignin in its molecular form. Oxidization, substitution by chlorine, and the addition of hydrogen chloride are important reactions that lead to substantial depolymerization of the lignin and to introduction of chlorine and various acidic groups into the lignin structure. As a result, part of the residual lignin from pulping is dissolved in the chlorination liquor.[92]

Reactions in the first caustic (alkali) extraction stage are less understood. In addition to ionizing the acidic groups formed during the C-stage, which facilitates solution of the chlorinated lignin, treatment with caustic causes a substantial removal of organically bound chlorine from the pulp formed during chlorination.[92]

COMPOSITION OF SPENT BLEACHING LIQUORS

Table II-2 presents the distribution of organically bound chlorine compounds by molecular weight for both chlorination (C) and caustic extraction (E) stages. These data indicate that about 70% of the organically bound chlorine is present as relatively high molecular-mass material (M > 1,000) in spent chlorination stage liquor; and, for E-stage liquors, about 95% of the organically bound chlorine falls in this class. Analyses indicate a major part of the high molecular weight material consists of cross-linked aliphatic compounds that are probably unsaturated. The high molecular weight compounds are probably biologically inactive because they cannot penetrate cell membranes in living organisms. However, the high molecular weight compounds break down chemically or biologically to form low molecular weight compounds which may have detrimental biological effects.[92]

About 30% of the organically bound chlorine in C-stage liquors and five% in extraction stage liquors is of low relative molecular mass (M < 1,000). These compounds have been classified into acidic, phenolic, and neutral compounds. Acidic compounds consist of fatty, hydroxy, dibasic, aromatic, and resin acids. The phenolic compounds consist of chlorinated phenols, guaiacols, vanillins, and catechols from softwood pulp bleaching and additionally chlorinated syringols and syringaldehydes from hardwood pulp bleaching. Chlorinated catechols occur primarily in C-stage liquors, while most chlorinated guaiacols and vanillins are found in spent E-stage liquors.[92,138]

Table II-2

SIZE DISTRIBUTION OF ORGANICALLY-BOUND CHLORINE FROM BLEACHING SOFTWOOD KRAFT PULP[92]

	Weight Percent	
Molecular Weight	Spent Chlorination Liquor	Spent Extraction Liquor
< 1,000	30%	5%
1,000 - 10,000	50%	20%
10,000 - 25,000	10%	20%
> 25,000	10%	55%

These compounds are formed from residual lignin.[92] The neutral fraction is composed primarily of methanol and various hemicelluloses, with comparatively less chlorinated material. The neutral chlorinated compounds include a number of saturated and unsaturated hydrocarbons, aldehydes, ketones and esters as well as chlorinated benzene derivatives and sulfur-containing compounds. Quantitatively, chlorinated acetones, chloroform, dichloromethane, and 1,1-dichloromethlysulfone predominate. The total quantity of chloroform and dichloromethane formed will be much higher if the bleaching sequence includes a hypochlorite (H) bleaching stage. Not all of the relatively low molecular mass compounds formed during bleaching have been identified.[92] Studies completed during the past few years have demonstrated that chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) are trace by-products of chlorine bleaching of kraft pulps. The most prevalent CDDs and CDFs found were 2378-TCDD and 2378-TCDF, respectively.[138]

III. REGULATION FOR CHLORINATED ORGANICS FROM PULP MILLS

Many countries of Western Europe [Austria, Denmark, Finland, Federal Republic of Germany(FRG), Norway and Sweden] as well as Canada and the United States already have or are presently in the process of developing regulations for the pulp and paper industry specifically dealing with the discharge of chlorinated organic compounds.[21]

EUROPE

Protection of the environment between European countries takes place through various conventions, often named after the city where the agreement was initially reached. Two of these conventions are the Helsinki-Convention and the Paris-Convention each of which has recently proposed regulations for the pulp industry regarding the discharge of chlorinated organics.[21] The proposals of these conventions as well as regulations, goals or proposed regulations for individual countries are as follows:

HELSINKI CONVENTION

Following a 15 February 1988 meeting of the Ministers of the Environment of the Baltic Sea Area a proposal was worked out that all new sulphite mills must meet immediately and all existing chemical pulp mills must meet before the year 2000 the following emission standards:[52,21]

Bleached Kraft Mills	2.0 kg AOX/metric ton pulp
Bleached Sulphite Mills	1.0 kg AOX/metric ton pulp

PARIS CONVENTION

The most recent Paris Convention meeting was held in London on January 17-19, 1989. At that meeting, Sweden presented the following proposal aimed at the reduction of chlorinated substances from the production of bleached pulp.[52]

1. As of January 1, 1994, the discharge of chlorinated organic substances should not, as an annual average, exceed the following values for each Contraction party's total production of:

Softwood kraft pulp bleached with chlorine chemicals:	2 kg AOX/metric ton
Hardwood kraft pulp bleached with chlorine chemicals:	1 kg AOX/metric ton
Sulphite pulp bleached with chlorine chemicals:	1 kg AOX/metric ton

2. The annual average values for each mill should, as a minimum, be based on one analysis a month. Analysis should be made on representative 24 hours, unsettled samples.

FEDERAL REPUBLIC OF GERMANY

The Federal Republic of Germany has recently passed new and revised emission standards which became effective on January 1, 1990. These regulation include an AOX standard of 1.0 kg/metric ton for sulphite pulp mill.[21] The FRG

no longer allows the operation of kraft pulp mills.[105] It should also be noted that no elementary chlorine is used in sulphite pulp bleaching in the FRG and generally oxygen delignification is utilized at these facilities.[21]

FINLAND

While Finland does not presently have regulations pertaining to the discharge of chlorinated organics, the government has an official goal for AOX of 1.5-2.0 kg/metric ton.[21] In 1989, the average treated effluent AOX discharge for Finnish bleached kraft mills was 2.86 kg/metric ton and the industry expects to reduce that value to 1.4 kg/metric ton by 1995.[21]

NORWAY

Chlorinated organic effluent standards for bleached pulp in Norway are: AOX (Kraft): 2 kg/metric ton; and AOX (Sulphite): 1 kg/metric ton.[52]

SWEDEN

Swedish regulations set out short term and long term requirement for the reduction of TOCl discharged to receiving waters. The short term requirement is 1.5 kg TOCl/metric ton to be achieved before the end of 1992.[21] The long term requirement is 0.1 kg TOCl/metric ton to be achieved before the end of 2010.[21]

CANADA

The Federal Government of Canada (Environment Canada) is currently in the process of developing regulations under the 1988 Canadian Environmental Protection Act (CEPA) to control the discharge of persistent toxics such as CDDs and CDFs.[71] A control regulation for CDDs and CDFs will be promulgated by the middle of 1990, following public consultation and ministerial review as required by law.[71] In addition, consideration is now being made as to what substances in addition to CDDs and CDFs should be controlled.[71] Also, at least four Canadian Provinces are in the process of establishment of regulations or issuing licenses dealing with the discharge of chlorinated organics. These provinces are, Alberta, British Columbia, Ontario and Quebec.

ALBERTA

The Province has no regulations pertaining to AOX, however, all existing and new bleached kraft mills will be licensed in the near future at 1.5 kg of AOX /metric ton (monthly average) and 1.4 kg of AOX/metric ton (monthly average), respectively.

BRITISH COLUMBIA

The Provincial Government is in the process of issuing new guidelines which will contain among other things an AOX limitation of 2.5 kg/metric ton by 1991 and 1.5 kg/metric ton by 1994.[21] While these standards have not been officially established, they are being incorporated into orders and permits and mills are designing systems to meets the limits and the dates established.

ONTARIO

In 1985, the Province of Ontario launched the MISA program (Municipal Industrial Strategy for Abatement) with the goal of elimination of persistent toxic compounds from the waters of the Province.[21,123] This program specifically addressed kraft mill effluents and resulted in the development of the following goals:

TABLE III-1

LEVELS OF ACHIEVEMENT FOR ONTARIO KRAFT PULP AND PAPER MILL EFFLUENTS[21,123]

Level		Organochlorines, kg AOX/ADMT
I	(Present level for all mills without treatment)	≥5.0
II	(Present level for mills with primary treatment)	<4.5
III	(Achieved within 1-3 years (1989-1991))	<2.5
IV	(Achieved by 1993)	<1.5

It is expected that these recommendations will be finalized in regulation in 1991, however as in British Columbia, companies are expected to institute programs now to meet the proposed limits.[21]

QUEBEC

An AOX limitation of 1.5 kg/tonne has been set by the Quebec Ministry of the Environment which is to be achieved by 1993.[193]

UNITED STATES

Under the Clean Water Act Amendment of 1987, EPA is presently in the process of revising the effluent limitations guidelines for the pulp and paper industry. The primary focus of this revision will be to develop Best Available Technology (BAT) limitations for 2378-TCDD for the chlorine bleached chemical pulping subcategories. In addition to 2378-TCDD, other toxic pollutants will be assessed and limitations established as appropriate. The present schedule for promulgation of the revised BAT regulations is July 1995.

III. MINIMIZATION OF CONTAMINATION FROM EXTERNAL SOURCES

WOOD SOURCES

A possible source of TCDD and TCDF in pulp mill effluents, sludges and pulps is from the use of contaminated chips from sawmills where lumber has been treated with chlorophenols. This possible source of contamination has not been specifically identified in U.S mills, however, it has been identified in several British Columbia mills.[162] In order to guard against this possible source of contamination, companies purchasing chips from unknown suppliers should either require certification that the chips are not contaminated or should perform periodic monitoring to insure that such contamination does not exist.

SELECTION AND USE OF ADDITIVES

Technology Description:

Numerous additives are used in the production of bleached pulp two groups of which have been shown to contain the dioxin and furan precursors DBD and DBF. These two groups of additives include defoamers and pitch dispersants. Defoamers are added to brownstock pulp slurries prior to pulp bleaching to prevent accumulation of entrained air which can lead to formation of foam that can interfere with downstream processing. Defoamers are made of kerosene, fatty acids, fatty alcohols and other hydrocarbons, or can be water-based. Recent research by the Pulp and Paper Research Institute of Canada (PAPRICAN) demonstrated that oil-based pulp mill additives, particularly brownstock defoamers are potential sources of unchlorinated dibenzofuran (DBF) and dibenzo-p-dioxin (DBD) and can result in elevated CDD and CDF levels in bleached kraft mill pulps.[33,119] Similar studies were carried out by Westvaco researchers. They added various defoamers to unbleached pulps at three to five times normal application rates resulting in elevated 2378-TCDD and 2378-TCDF levels in chlorinated pulps.[108] Findings of unusually high levels of 2378-TCDF at a number of mills in the 104 Mill Study have been linked to use of contaminated oil-based defoamers. In some cases, the levels of 2378-TCDF found at these mills exceeded median values for all mills by more than two orders of magnitude. The technology to address this problem is to switch to a non-contaminated defoamer.

Pitch dispersants are added to the pulp prior to washing similar to brown stock defoamers. Generally these dispersants are oil based. The majority of investigation work in the industry has been directed toward defoamers, however, recently a number of facilities have identified pitch dispersants as sources of precursors and have therefore either discontinued there use or found alternative agents which had lower levels of precursors.

Effectiveness:

Where changes have been made from contaminated to clean defoamers, the 2378-TCDF levels have been reduced to levels well within those encountered at the majority of mills in the 104 Mill Study. The impact on formation of 2378-TCDD has been less dramatic. Studies performed at Western Pulp in Canada showed an approximate 90%

reduction in the content of TCDF in the pulp and the effluent when they switched from an oil based defoamer with a DBF level of 9500 ppb to a defoamer made with non-recycled oil and a DBF level of <200 ppb.[162] Studies performed by James River on various defoamers revels that there can be a substantial difference between the level of DBF in defoamers ranging from 11 to 2230 ppb.[136] See **Table IV-1.**

TABLE IV-1

DIBENZOFURAN ANALYSIS OF DEFOAMERS[136]

Sample Number	Materials and Description	DBF (ppb)
1	CZ 792 1 yr. composite 1988	66
2	CZ 702 1 yr. composite 1988	350
3	CZ 710 H_2O based; 1 yr. composite 1988	11
4	CZ 702 3 runs, 10/88	497
5	CZ 792 Batch 11/14/88	138
6	CZ 710 H_2O based; batch 11/15/89	17
7	Oil in tank 26 11/17/88 (Witco)	520
8	Oil in tank 32 11/17/88 (Witco)	539
9	Oil as delivered 11/21/88 (Witco)	2230
10	Oil as delivered 12/5/88 (Witco)	833
11	Oil as delivered 3/1/89 (Chevron)	128
12	Oil as delivered 3/20/89 (Chevron)	32
13	Sample 12 spiked with 50 ppb DBF	72

While this research has led to the reduction of CDD and CDF being discharged by the industry, recent research indicates that precursors other than DBD and DBF for CDDs and CDFs exist.[108]

Installations:

Numerous mills have made the conversion to low precursor additives as evidenced by recent submissions made to the Agency relating changes made since samples were obtained for the 104 Mill Study.

Implementation:

Inasmuch as no significant process modifications or equipment changes are necessary, the implementation time to change from contaminated to clean additives should not exceed the time necessary for purchase and delivery of replacement chemicals.

Costs:

The literature contains no information regarding the cost of clean vs. contaminated additives. However, it is not thought that the the conversion to clean additives would result in a significant cost impact.

References:

33, 108, 119, 136, 141, 189

V. MINIMIZATION ON CONTAMINATION THROUGH PROCESS CHANGES - PULPING

AVAILABLE TECHNOLOGIES

EXTENDED DELIGNIFICATION

Technology Description:

This technology involves extending the kraft cooking process to produce a brownstock pulp with lower lignin content, thus reducing the demand for bleaching chemicals. Extended cooking involves modifying the process to obtain a more even alkali profile through the digesters, combined with partial countercurrent operation.[16] The pulp is digested longer either in continuous or batch modes, with modified time-temperature-alkaline cycles to reduce adverse impacts of extended pulping on pulp quality. As of the present date, the two most used extended delignifications systems are Modified Continuous Cook and Rapid Displacement Heating.

The Modified Continuous Cook (MCC) process was developed by Kamyr for more selective removal of lignin in continuous digesters. The process is based on principles developed by STFI in the late 1970's which include low effective alkali concentrations at the beginning of the cook and low concentrations of lignin at the end of the cook. This is accomplished by splitting the addition of the cooking liquor such that fresh liquor is introduced near the end of the cooking cycle and is circulated counter-currently to the chip flow, to maintain alkalinity. Using this process, the kappa number of unbleached pulp can be reduced from 30-32 for conventional cooking to 22-25 for softwood and from the conventional cooking of 16-18 to 12-14 for hardwood.[121]

Rapid Displacement Heating (RDH) is a low energy cooking process for batch digesters developed by Beloit Corporation. In RDH, liquor profile chemistry is controlled to subject the incoming wood chips first to recycled black liquors which neutralize the acidity of the incoming wood. In this stage, the more soluble fractions of the extractives, lignin, and oligomeric hemicelluloses are dissolved and removed. This accounts for a net lower alkali charge during the high temperature portion of the RDH cook, which in turn results in improved strength and other pulp characteristics. Softwood brownstock kappa numbers as low as 15-18 and hardwood kappa numbers as low as 8-10 can be attained with this process without hardware modifications.[12]

Effectiveness:

Reduced consumption of active chlorine following extended delignification has been documented in pilot tests and at full scale.[6,16] Given that the amount of chlorine required in prebleaching is directly related to the lignin content of the brownstock pulp, any process that results in incremental lignin removal prior to bleaching will result in reduced quantities of chlorinated organics formed. A comparison of untreated effluent from a bleached kraft mill for different combinations of process controls including extended delignification is provided in **TABLE V-1.**

TABLE V-1

CHARACTERISTICS OF UNTREATED EFFLUENT FROM A BLEACHED SOFTWOOD KRAFT PULP MILL SHOWS ADDITIVE EFFECTS FOR DIFFERENT IN-PROCESS MODIFICATIONS[121]

	CASE A	CASE B	CASE C	CASE D
Flow, m^3/a.d.m.ton	50-55	50-55	50-55	50-55
BOD_5, kg/a.d.m.ton	28	22	20	20
COD, kg/a.d.m.ton	100	70	55	55
Color, kg/a.d.m.ton	300	100	80	65
AOX, kg/a.d.m.ton	7.9	4.7	3.6	1.9

Case A is state-of-the-art kraft mill employing conventional process technology.
Case B is Case A with oxygen delignification.
Case C is Case B with modified cooking (extended delignification).
Case D is Case C with 70% chlorine dioxide substitution.

This comparison shows that extended delignification is effective in removing chlorinated organics, measured as AOX, as well as other pollutants of concern. Another study showed that formation of TOCl is reduced from 6-7 kg/ton of pulp to 4.5-5 kg/ton of pulp with extended delignification.[22]

In addition to the effluent reduction benefits, RDH pulping is reported to result in up to a ten percent increase in pulp strength; a 10-15% reduction in pulping cycle time; a 65% reduction in steam demand; and a two to three GJ/ADMT energy savings.[12,152] Extended delignification has the added benefit of affecting additional lignin removal with recoverable pulping chemicals as opposed to consumable chemicals used in conventional bleaching.

Installations:

The number of extended delignification installations is growing rapidly. Reference lists for facilities where MCC and RDH installations are planned, under construction or in operation are provided in **Table V-2** and **Table V-3**, respectively.

Implementation:

Extended delignification is compatible with conventional processes. Pulp quality is reported to be generally equal to or better than conventionally cooked pulp. Reduced pulp yield and viscosity have been reported to be associated with kappa number reduction; however, a gain in viscosity has also been reported.[6,16] Retrofitting existing batch

TABLE V-2

WORLDWIDE EXTENDED DELIGNIFICATION - MODIFIED CONTINUOUS COOK (MCC) REFERENCE LIST[a]

CUSTOMER	LOCATION	PRODUCTION TPD	FURNISH	START-UP
Enso-Gutzeit OY	Varkaus, Finland	450	HWD/SWD	1983
Metsa-Botnia AB, OY	Aanekoski, Finland	1210	HWD/SWD	1987
Consolidated Papers Inc.	Wisconsin Rapids, WI	400	HWD/SWD	1987
Domtar Inc.	Windsor, Que.	1145	HWD/SWD	1987
Alicel[b]	Alizay, France	900	HWD	1987
Federal Paper Board Co., Inc.	Augusta, GA	770	HWD/SWD	1987
AB Iggesunds Bruk	Iggesund, Sweden	690	SWD	1988
Kemi OY	Kemi, Finland	880	HWD/SWD	1988
Longview Fibre Company	Longview, WA	1060	SWD	1988
Korsnas AB	Gavle, Sweden	1160	HWD/SWD	1989
Oji Seishi	Kasugai, Japan	880	SWD	1989
Champion International Corp.	Hinton, Alta.	1460	SWD	1989
Tasman Pulp and Paper LTD	New Zealand	550	SWD	1989
AB Iggesunds Bruk	Iggesund, Sweden	700	HWD	1989
Howe Sound Pulp and Paper LTD	Port Mellon, B.C.	1450	SWD	1990
Federal Paper Board Co., Inc.	Augusta, GA	1520	HWD	1990
Daishowa Canada[b]	Peace River, Alta.	1360	HWD/SWD	1990
Weyerhaeuser Company	Columbus, MS	1575	HWD/SWD	1990
Aracruz[b]	Aracruz, Brazil	2075	HWD	1990
Stone Container Corp.	Pt. Wentworth, GA	865	HWD	1991
Bahia Sul[b]	Entre Rios, Brazil	1500	HWD	1991
Union Camp Corporation[b]	Eastover, SC	1250	HWD	1991
Champion International Corp.	Courtland, AL	1180	SWD	1991

[a] Source: Kamyr, Inc.
[b] Future Provision

digestion systems with extended delignification would require enough additional space for the installation of a tank farm. To date, the majority of RDH digesters in operation have been retrofits. Retrofitting an existing continuous digester with MCC, however, is not as feasible. Of some 180 continuous digesters in North America, less than ten could be retrofitted with MCC according to the supplier.[137]

TABLE V-3

WORLDWIDE EXTENDED DELIGNIFICATION - RAPID DISPLACEMENT HEATING (RDH) REFERENCE LIST[a]

START-UP	MILL/LOCATION	DIGESTERS	PRODUCTION	PULP
1985	Joutseno Pulp Joutseno Finland	4 New - 200 m^3 - SS Clad 7 Retrofit - 140 m^3 - Mild Steel	950 ADT/D	Bleachable Grades Kappa Range 20 - 32 Softwood & Hardwood
1987	Nymolla AB Nymolla Sweden	4 Retrofit - 380 m^3 - Solid SS 5 Retrofit - 250 m^3 - Solid SS	860 ADT/D	MG - Sulfite Paper Grade Softwood
1988	S.D. Warren Westbrook, ME USA	4 New - 200 m^3 - SS Clad	450 ADT/D	Bleachable Grades Kappa Range 8 - 10 Hardwood
1989	Bowaters Southern Paper Calhoun, TN USA	8 New - 200 m^3 - SS Clad	1200 ADT/D	Bleachable Grades Kappa Range 18 - 30 Softwood & Hardwood
1989	Fletcher Challenge Crofton, B.C. Canada	8 Retrofit - 168 m^3 - SS Overlay	850 ADT/D	Bleachable Grades Kappa Range 26 - 30 Softwood
1990	Chung Hwa Paper Corp. System I Hualien, Taiwan	5 Retrofit - 120 m^3	500 ADT/D	Bleachable Grades Kappa Range 16 - 24 Mixed Tropical Hardwood
1990	Willamette Industries Bennettsville, SC USA	6 New - 200 m^3 - Mild Steel with SS Nozzles	860 ADT/D	Bleachable Grades Kappa Range 16 - 24 Softwood & Hardwood
1990	Chung Hwa Paper Corp. System II Hualien, Taiwan	5 Retrofit - 120 m^3	500 ADT/D	Bleachable Grades Kappa Range 16 -24 Mixes Tropical Hardwood

[a] Source: Beloit Corporation

Implementation time for a MCC system was provided by the supplier to be approximately 24 months from the order date to start-up.[137] Implementation time for a RDH system was provided by the supplier to be approximately 16 months for design, construction and installation.[153] Present delivery time for the long lead items for RDH is running around one year.[153]

Costs:

For a new MCC digester (1200 ADST/day) the equipment cost would be $15 to $16 million with the installed cost being $30 to $32 million.[137] Of this cost, about $1.5 to $2.0 million would be related to the MCC portion.[137] Retrofit costs for MCC are not appropriated as discussed above. No operating costs were found for the MCC process.

For RDH systems, the capital cost would be approximately $1.5 million for each digester plus $5 million for the tank farm with a turnkey cost being approximately three times as much.[153] For a retrofit system, the only difference would be in the cost of the digester which at the present date was estimated to be $600,000 for a 700 cubic foot stainless steel clad digester.[153] With respect to operation and maintenance costs, the supplier of RDH systems state that the system has an 18 month payback based on steam savings, a better quality pulp, less evaporation required due to higher solids in the washwater and a reduction (approximately 50%) in bleaching chemicals.[153]

References:

6, 12, 21, 42, 54, 72, 73, 85, 87, 89, 95, 96, 106, 109, 110, 114, 116, 121, 132, 137, 139, 144, 152, 153, 166, 173, 178, 181, 182

OXYGEN DELIGNIFICATION

Technology Description:

Oxygen delignification (OD), also referred to as oxygen bleaching, developed into a commercially feasible process in the late 1960s and early 1970s. The first installation of OD was in South Africa, however, until recently, the majority of installations have been in Sweden where oxygen delignification has been utilized as an economical alternative to secondary treatment, and in Japan, where oxygen costs are low. Oxygen delignification is a pulp treatment stage following final brownstock washing, but prior to bleaching with chlorine or chlorine derivatives. In the process, brownstock pulp is treated with oxygen under pressure in an alkaline environment to remove additional lignin and to alter other color producing material. Although oxygen delignification systems are often co-located with bleacheries, they are chemically linked to the digestion process in that washwaters from OD stages are returned to the chemical recovery system along with waste cooking liquor for recovery of inorganic chemicals and heat value from the organic load removed from the pulp. This removal of organic load accomplished in OD reduces the downstream chemical requirements for pulp bleaching, and attendant formation of chlorinated organics.[22]

Oxygen delignification was originally developed as a high consistency (25-28%) process, however with the development of the high shear mixer, medium consistency (10-12%) operation became feasible.[8] Consistency selection is dependent on capital cost, the degree of delignification and steam, alkali and power consumption. High consistency systems are slightly higher in cost than medium consistency systems due to the need for a pulp press prior to the reactor.[8] Delignification in the two systems is comparable with the high consistency systems running in the range of 45-50% as compared to medium consistency systems which run in the range of 40-45%.[8] Steam and alkali consumption are higher in the medium consistency systems whereas power consumption is higher in high consistency systems.[8]

OD is compatible with other new technologies aimed at reducing bleach plant effluents and OD bleached pulps are reported to be equal or superior to conventionally bleached pulps with respect to tear strength, brightness stability, pitch removal, beating energy and cleanliness.[8,75] Because approximately one-half of the original residual lignin is removed during the oxygen stage, the number of subsequent conventional bleaching stages may be reduced. It is now well-established commercially that for bleached softwood kraft pulp, a four-stage sequence such as C/DEHD following oxygen delignification is sufficient to attain 90+ GE brightness, and that a three-stage sequence such as CED is adequate to achieve an 85 to 90 GE brightness level.[75]

Effectiveness:

The environmental benefits associated with OD have been documented in many publications. These benefits accrue from two facts. The first is that by reducing the amount of lignin carried forward with the pulp, levels of BOD, COD and color are reduced in the effluent discharged. This reduction has been reported to be 40-55% for BOD, 45-55% for COD and 60-75% for color.[8] Secondly an oxygen delignification stage placed ahead of chlorination reduces

the amount of chlorine conventionally required by about 50% and reduces the amount of chlorine dioxide required for a given brightness, resulting in a reduction in the amount of chlorinated organics discharges.[38,57] A review of **Table V-1** presented earlier shows that OD reduces AOX levels from 7.9 kg/ADMT to 4.7 kg/ADMT (41% reduction).[121] Another study shows that TOCl formation from a kraft softwood pulp bleach plant was reduced from 5 to 5.5 kg/metric ton of pulp to 2.5 to 3.5 kg/metric ton of pulp (35-50%).[58] A third study reported a reduction in total organic chloride from 5.4 kg /ton of pulp using a D(30)/C(70)EDED sequence to 0.7 kg /ton of pulp using a ODEoD sequence, for bleaching softwood Kraft pulp.[61]

Use of OD systems has not completely eliminated formation of 2378-TCDD and 2378-TCDF, but at three U.S. mills using OD systems levels found tend to be in the lower range of values encountered at U.S. mills. CDD and CDF data from three mills with oxygen delignification are provided in **Table V-4.** The CDD and CDF levels for most of the effluents and pulp sampled were below the detection level.

Additional data related to oxygen delignification in combination with other processes such as chlorine dioxide substitution will be presented in subsequent sections.

Installations:

According to a recent article, oxygen delignification systems corresponding to approximately one third of the world bleached kraft pulp production have now been sold.[196] The first OD installation was started up at the SAPPI mill in South Africa in 1970. Since that date, the world's annual production capacity has steadily increased. A November 1987 TAPPI Journal article reported that since 1970, there have been 44 oxygen delignification process startups with a 1988 anticipated annual production capacity in excess of 10 million metric tons per year.[8] The same article broke down the production as of that date as 92% kraft, 60% softwood, 60% high consistency, 50% in Scandinavia and Europe, 20% in North America and 20% in Japan.[8] To illustrate the extant to which OD has been implemented in Sweden, production and process data are presented in **Table V-5.** From this table it can be seen that at the present date 86% of Swedish permitted bleached kraft production is subjected to oxygen delignification and that by the end of 1990 it will be 88%.

Those facilities that are presently planned, under construction or in operation are presented in **Table V-6.** A review of this listing shows that the 1990 anticipated annual production capacity will be in excess of 14 million metric tons per year, that the majority of production is still kraft softwood, the majority of new installations are in North America and that since about 1984, the vast majority of installations are based on medium consistency.

Implementation:

Compatibility With/Impact on Pulp and Other Processes

Several authors have compared conventional bleaching processes with a process having an oxygen delignification stage. Impacts on pulp and processes presented in the literature include those related to the recovery system, chemical make up and usage, product quality, process control and compatibility. Routing the wash water from the

TABLE V-4

DIOXIN/FURAN DATA FOR THREE BLEACHED KRAFT MILLS WITH OXYGEN DELIGNIFICATION[201]

	MILL 1	MILL 2	MILL 3
WOOD TYPE (LINE 1)	SWD	SWD	HWD
(LINE 2)	-	HWD	HWD
OXYGEN DELIGNIFICATION (LINE 1)	YES	YES	NO
(LINE 2)	-	YES	YES
DIOXINS & FURANS			
BLEACHED PULP (LINE 1)			
2378-TCDD, ng/l	ND(1.5)	ND(0.8)	ND(0.4)
2378-TCDF, ng/l	NQ(14)	2.11	2.71
BLEACHED PULP (LINE 2)			
2378-TCDD, ng/l	-	ND(1.0)	ND(0.7)
2378-TCDF, ng/l	-	ND(1.2)	ND(0.6)
Eo FILTRATE (LINE 1)			
2378-TCDD, pg/l	ND(8)	102	ND(5)
2378-TCDF, pg/l	ND(13)	114	95
Eo FILTRATE (LINE 2)			
2378-TCDD, pg/l	-	ND(3)	ND(5)
2378-TCDF, pg/l	-	ND(3)	42
WASTEWATER INFLUENT			
2378-TCDD, pg/l	ND(8)	ND(4)	ND(3)
2378-TCDF, pg/l	ND(8)	NQ(7)	ND(4)
FINAL EFFLUENT			
2378-TCDD, pg/l	ND(10)	NQ(2)	ND(8)
2378-TCDF, pg/l	ND(10)	ND(12)	ND(8)

oxygen delignification process to the recovery system increases the solids load to the chemical recovery furnace, typically by 3-5% and up to 10% if existing brownstock washing is not efficient.[8,31,75] Although recovery of these dissolved solids and lignin contribute to steam generation, the capability of existing recovery furnaces to accept the additional solids loading is uncertain. Possible solutions for those cases where recovery furnaces could not accept additional solids loading would be through the use of anthraquinone and/or polysulfide pulping which is covered in more detail in subsequent sections of this report.[158] Installation of an oxygen stage into an existing conventional system would require caustic for the oxygen stage which is usually met through use of oxidized white liquor. This results in an increased load on the causticizing plant and lime kiln on the order of 3-5% and increasing evaporation

steam requirements on the order of 0-4% for high consistency and 4-10% for medium consistency oxygen bleaching;[8,57] While the oxygen delignification process requires a source of caustic, chemical usage (primarily chlorine and caustic) across the entire facility would be reduced.[8] Oxygen bleaching has a superior ability to decrease shive content and the oxygen bleaching stage is less sensitive (than conventional stages) to kappa number changes in the incoming pulp allowing the control of kappa number within narrow limits.[75] Oxygen bleaching is compatible with other chlorine-free bleaching processes being developed.[75]

TABLE V-5

EXTENDED DELIGNIFICATION, OXYGEN DELIGNIFICATION AND BIOLOGICAL WASTEWATER TREATMENT AT SWEDISH BLEACHED KRAFT PULP MILLS[116]

	MAXIMUM ALLOWED PRODUCTION, 1000 METRIC TONS/YEAR						
MILL LOCATION	TOTAL	SOFTWOOD	HARDWOOD	EXTEN. DELIG.	OXYGEN DELIG.	BIO. TREAT.	ED+OD +BIO.
Aspa Bruk	115	115	-	-	115	-	-
Gruvon	310	210	100	-	310	310	-
Husum	690	345	345	-	690	-	-
Iggesund[a]	325	217	108	325	217	325	217
Karlsborg	290	290	-	290	-	290	-
Korsnas	325	244	81	325	325	325	325
Monsteras	350	175	175	-	350	350	-
Morrum	375	150	225	-	375	-	-
Norrsundet	252	252	-	-	252	-	-
Skoghall	110	110	-	-	-	110	-
Skutskar	500	360	140	-	360	-	-
Skarblacka	150	[b]	[b]	-	150	150	-
Vallvik	220	220	-	-	220	-	-
Varo	300	300	-	300	300	-	-
Ostrand	322	232	90	-	322	-	-
TOTALS	4,634			1,240	3,986	1,860	542
%	100			27	86	40	12

[a] Oxygen delignification on both lines to be operational in 1990.

[b] No decision regarding production split between softwood and hardwood.

TABLE V-6

WORLDWIDE OXYGEN DELIGNIFICATION REFERENCE LIST[a]

COMPANY	LOCATION	COUNTRY	ADMT/D	WOOD	CONSIS-TENCY	BLEACH SEQUENCE	START DATE
		KRAFT					
Alberta Pacific	Athabasca, ALB	Canada	1400	SWD/HWD	Med.		1992
ASSI Karlsborg	Karlsborg	Sweden	1025	SWD	Med		1990[b]
Billerud AB	Gruvon	Sweden	500	SWD	High	OC/DEDED	1972
Bowaters-Southern	Calhoun, TN	USA	1180	SWD/HWD	Med.	OC/DEoD	1990
Canadian Forest Products	Pr. George, BC	Canada			Med.		
Celgar Pulp Company	Castelgar, BC.	Canada	1320				1992
Cellulose d'Aquitaine	St-Gaudens	France	500	HWD	High	OCEDED	1973
Cellulose des Ardennes	Rouvroy	Belgium	520	HWD	Med.		1985
CELPAG	Ribeirau Preto	Brazil	500		High	OC/DEoD	1979
Celulosa Arauco	Arauco	Chile	750		Med.		1989[b]
Celulosa del Pacifico SA	Mininco	Chile	1050		Med.		1989[b]
Champion International	Canton, NC	USA	1600	SWD	Med.		1992
Champion International	Courtland, AL	USA	1150	SWD/HWD	Med.		1991
Champion International	Hinton, ALB	Canada	1300	SWD	Med.		1987
Champion International	Pensacola, FL	USA	560	SWD	Med.	OC/DEoD	1987
Champion International	Pensacola, FL	USA	730	HWD	Med.	OC/DEoD	1986
Champion International	Quinnesec, MI	USA	1150		Med.		1990
Chesapeake	West Point, VA	USA	550	HWD	High	C/DOD	1972
Chuetsu Pulp Ind. Co., LTD	Sendai	Japan	550	HWD/SWD	Med.	OCHpHEpD	1986
Chung Hwa Pulp Corp.	Hualien Hsien	Taiwan	445		Med.		1987
Chung Hwa Pulp Corp.	Hualien Hsien	Taiwan	445		Med.		1987
Consolidated Paper	Wisc. Rapids, WI	USA	450	HWD	Med.	OC/DEoD	1980
Daishowa	Shiraoi	Japan	550	HWD	High	OCEHD	1975
Daishowa	Shiraoi	Japan	400	HWD	Med.		1986
Daishowa	Suzukawa	Japan	620	HWD	Med.		1986
Daishowa	Peace River, ALB	Canada	960	SWD	Med.		1990
Eddy Forest Products	Espanola, ONT	Canada	500	SWD	High	OC/DEoHD	1977
Eddy Forest Products	Espanola, ONT	Canada	500	HWD	High	OC/DEHD	1980
Empresa Nacional deCelulosas	Huelva	Spain	965	HWD	Med.	OC/DEoD	
Fiskeby AB	Skarblacka	Sweden	510	HWD/SWD	Med.		1986
Hokuetsu Paper	Niigata	Japan	480	HWD	Med.	OCEHD	1986
Hokuetsu Paper	Niigata	Japan	600	HWD	Med.		1988[b]
Howe Sound P.& P., LTD	Port Mellon, BC	Canada	1000	SWD	Med.		1990
Iggesunds Bruk AB	Iggesund	Sweden	900	HWD/SWD	Med.	OD/CEopDEpD	1990
International Paper Company	Texarkana, TX	USA					
James River-Marathon, LTD	Marathon, ONT	Canada			Med.		
Jujo Paper	Kushiro	Japan	600	SWD	High	OH	1975
Jujo Paper	Yatsushiro	Japan	550	HWD	Med.		1989
Kemi OY	Kemi	Finland	1055		Med.		1989[b]
Kishu Paper	Shiraoi	Japan	530	HWD	Med.	OCEHD	1987
Korsnas AB	Gavle	Sweden	1050	HWD/SWD	Med.	OC/DEoDD	1987
Korsnas AB	Marmaverken	Sweden	100		Med.		1983
Louisiana-Pacific Corp.	Eureka, CA	USA	680	SWD	Med.	OC/DEoDED	1989
Mitsubishi	Hachinohe	Japan	1100	HWD	Med.		1988[b]
Mitsubishi	Shirakawa	Japan	300	HWD	Med.		1986
MoDoCell AB	Husum	Sweden	1000	SWD	High	OC/DEDED	1977
Munksjo AB	Aspa	Sweden	380	SWD	High	OC/DEDED	1973
NCB Vallvik	Vallvik	Sweden	600	SWD	High	OC/DEDED	1978

TABLE V-6 (CON'T)

WORLDWIDE OXYGEN DELIGNIFICATION REFERENCE LIST[a]

COMPANY	LOCATION	COUNTRY	ADMT/D	WOOD	CONSIS-TENCY	BLEACH SEQUENCE	START DATE
New Zealand Forest Prods.	Kinleith	New Zealand	750		Med.		1989[b]
Norrsundet Bruks AB	Norrsundet	Sweden	1000	HWD/SWD	High	OC/DEoOd	1983
Oji Paper	Ebetsu	Japan	650	HWD/SWD	Med.	OD/CEHD	1986
Oji Paper	Tomakomai	Japan	550	SWD	Med.	OH	1985
OY Schauman	Jakobstad	Finland	900	SWD	Med.		1987
Polser Zellstoff	Pols	Austria	630	SWD	Med.	OD/CEDED	1984
Pope & Talbot Pulp Co.	Halsey, OR	USA		SWD			
Port Westward Pulp	Pt. Westward, OR	USA	750	SWD	Med.	OC/DEoDD	
Potlatch Corporation	Lewiston, ID	USA	1000	SWD	High	OC/DEoD	1991
Procter & Gamble	Oglethorpe, GA	USA	1000	SWD	High	OD/CEoD	1980
Proctor & Gamble	Gr. Prairie, ALB	Canada			Med.		1991
PT Indah Kiat Pulp & Paper	Perawang	Indonesia	525		Med.		1988[b]
Repap Manitoba Inc.	The Pas, MAN	Canada	1200		Med.		
Sanyo-Kokosaku Pulp Co.	Iwakuni	Japan	450	HWD	Med.		1988[b]
Sappi	Enstra	S. Africa	200	SWD	High	ODED	1970
Sappi	Enstra	S. Africa	500	HWD	High	ODED	1978
Sappi	Ngodwana	S. Africa	575	SWD	High	OD/CED	1985
SCA Pulp AB	Ostrand	Sweden	1000	HWD/SWD	High	OC/DEDED	1980
Simpson Paper Company	Fairhaven, CA	USA	600	SWD	Med.		1989
Sodra Skogsagarna AB	Monsteras	Sweden	1000	HWD/SWD	High	OC/DEDED	1981
Sodra Skogsagarna AB	Morrum	Sweden	420	SWD	Med.		1989
Sodra Skogsagarna AB	Morrum	Sweden	700	HWD	Med.		1989
Sodra Skogsagarna AB	Varobacka	Sweden	950	SWD	Med.		1985
Stora Cell AB	Skutskaer	Sweden	650	SWD	High	OC/DEDED	1977
Stora Cell AB	Skutskaer	Sweden	650	SWD	High	OC/DEDED	1978
Suzano de Papel e Celulose	Suzano	Brazil	1365	HWD	Med.		1989
Taio Seishi Paper	Mishima	Japan	525	SWD	Med.	OCEHDD	1986
Taio Seishi Paper	Mishima	Japan	665	HWD	Med	OD/CEoHED	1984
Union Camp Corporation	Eastover, SC	USA	650	HWD/SWD	High	OC/DED	1984
Union Camp Corporation	Eastover, SC	USA	1100		Med.		1989[b]
Union Camp Corporation	Franklin, VA	USA	800	HWD	High	OC/DED	1981
Ust Ilimsk	Ust Ilimsk	USSR	800	SWD	High	OD/CEHDED	1979
V/O Prommash	Svetogorsk	USSR	455	HWD	Med.	ODEDED	1985
Weyerhaeuser Company	Columbus, MS	USA	1200		Med.	OC/DEoDD	1990
Willamette Industries	Bennettsville, SC	USA	760	SWD/HWD	Med.	OC/DEoD	1990
Xin Hua Paper Mill	Shanghai	China	75	Straw	Med.		1988[b]
Zaklady Celulozowo	Kwidzyn	Poland	600	SWD	High	OC/DEHD	1978
		SULFITE					
Bayrische Zellstoff	Kelheim	FRG	160	SWD	High	OEDH	1979
Flambeau Paper	Park Falls, WI	USA	200	HWD	Med.	OH	1987
Hannoversche Papierfabriken	Alfeld-Gronau	FRG	250	SWD	Med.	OCEH	1986
Hunsfos	Hunsfos	Norway	130	HWD/SWD	High	OCEHH	1979
Industrias Forestales SA	Nacimento	Chile	750		Med.		1989[b]
PWA Waldhof	Mannheim	FRG	185	SWD	Med.	POsPOaHH	1986
Rauma-Repola	Rauma	Finland	450	SWD	Med.	OCEDH	1983
Severomoravske Celulozky NP	Paskov	Czech.	660	SWD	High		1984
Tofte Industrier	Tofte	Norway	700	SWD	Med.		1983
Weyerhaeuser Company	Cosmopolis, WA	USA	400	HWD/SWD	Med.		1990

TABLE V-6 (CON'T)

WORLDWIDE OXYGEN DELIGNIFICATION REFERENCE LIST[a]

COMPANY	LOCATION	COUNTRY	ADMT/D	WOOD	CONSIS-TENCY	BLEACH SEQUENCE	START DATE
		SPECIALITY					
Korsnas AB	Gavle	Sweden	100	HWD/SWD	Med.		1983
M. Peterson & Son	Moss	Norway	150	SWD	Med.		1980

[a] 8, 116, 123, 137, 155, 157
[b] Order date

Availability

High consistency oxygen bleaching systems require that most of the equipment be fabricated from stainless steel to avoid corrosion.[75] Prices and work schedules could be affected by availability of stainless steel. One reference claims that the stainless steel resource is very tight and that not even Asian sources, which are used by the industry, can meet the demand.[4] The majority of recent oxygen bleaching system installations have been medium consistency. This trend has been influenced, to some degree, by the limited number of high consistency equipment suppliers in certain geographic regions.[8]

Time to Implement

Implementation time will be highly site specific. Where recovery boiler capacity and space are not limiting factors, installation of an OD stage to an existing bleach line can be accomplished in approximately two years. Information obtained from a consulting firm related that six months were required for study with 20 months for installation.[191] However, if major recovery system modifications are necessary, the implementation time for the total system could take up to three years.

Limitations

Limitations identified in the literature are as follows: (a) Cellulose degradation. High consistency oxygen delignification must be limited to approximately 50% of residual lignin in order to avoid excessive pulp strength reduction;[78] (b) Brightness. There is less of a margin than conventional CEDED process, in acquiring high brightness (90% ISO) without deterioration in pulp strength.[61] Brightness of 85-87 ISO can be achieved with short sequence bleaching, however, one source reports that for high brightness pulp, 89-90 ISO, that five stages of bleaching may be required.[72] Another source reports that a pulp brightness of 90 ISO can be achieved on softwood with OC/DE_oD bleaching.[57]

Costs:

The literature contains limited capital cost data for oxygen delignification systems. A large amount of data, however, is available with respect to operational costs of OD systems especially as these costs compare to conventional bleach systems.

Capital Costs

Capital costs for a bleaching sequence including an oxygen stage are reported to cost more than conventional sequences, however, for a new mill these costs are offset by reduced capital costs for other processes such as brownstock washing, chemical preparation, power boiler and effluent wastewater treatment facilities.[57] One literature source reported an installed capital cost of $8.8 million for a 500 ton/day OD system.[73] This cost compares favorably to a suppliers estimate of installed capital costs for a new 500 ton per day OD facility of $9-11 million and for new 1000 ton per day facility of $14-16 million.[112] A second supplier related that the installed cost for a 1000 ADMT/day medium consistency OD facility would range from 80,000,000 to 100,000,000 SEK ($13-16 million).[157] Another estimate of installed capital costs was obtained from a large consulting firm ranging from $13.5 million for a hardwood medium consistency OD system to $19.5 million for a softwood high consistency OD system.[191] These costs, based on several installations are for a 600 air dried bleached tons per day facility and include both pre and post washing in addition to the oxygen delignification system.[191] In comparing system costs, it should be pointed out that high consistency systems are more expensive than a similar sized medium consistency system due to need for a pulp press costing in the range of $1-4 million.[8] In addition to these estimated costs, costs for three specific facilities are provided in **TABLE V-7.**

TABLE V-7

OXYGEN DELIGNIFICATION CAPITAL COSTS*

COMPANY	LOCATION	PRODUCTION, ADMT/D	CONSISTENCY	CAPITAL COST, $1000
Louisiana-Pacific Corporation	Samoa, CA	680	Medium	8,000
Simpson Paper Company	Fairhaven, CA	600	Medium	11,500
Weyerhaeuser Company	Cosmopolis, WA	400	Medium	9,000

* Costs taken from news articles and information provided to EPA by the companies.

Operating Costs

Chemical savings associated with oxygen delignification are proportional to lignin reduction.[31] Oxygen is the least expensive chemical among the oxidizing agents used for the bleaching of pulps. In addition, the production of oxygen requires one eighth the energy to make the chemically equivalent amount of chlorine.[31]

Several references concur that when compared to a conventional sequence, a kraft softwood bleach line containing an oxygen delignification stage would consume approximately the same amount of energy (steam and electricity), consume less chemicals, and decrease wastewater treatment costs.[5,11,57,76] Specifically, one source reported operating cost savings of $16/ton of softwood pulp at 90 ISO brightness using high consistency OD and a bleaching sequence of OC/DEoD vs. conventional C/DEDED bleaching.[57] Another source reported annual cost savings of $8.55/ton for softwood and $3.16/ton for hardwood.[191] These figures agree fairly well with a third source which related cast savings of $9 an $4/metric ton of softwood and hardwood pulp, respectively.[8]

After depreciating capital cost and incorporating operating and treatment costs savings, one source reports that the use of oxygen bleaching in both an existing and a new plant results in a lower cost per ton of pulp.[76] Using a installed capital cost of $17 million for a 1000 ton/day facility and a operational cost savings of $9/ton results in a return on equity of around seven years.

References:

3, 4, 5, 8, 10, 11, 14, 15, 21, 22, 23, 29, 31, 33, 36, 38, 40, 43, 49, 55, 56, 57, 59, 60, 61, 63, 64, 65, 66, 69, 70, 72, 73, 74, 75, 76, 80, 83, 85, 90, 91, 92, 93, 95, 96, 98, 109, 112, 116, 120, 121, 132, 133, 140, 142, 144, 149, 155, 157, 158, 160, 165, 166, 168, 169, 170, 171, 173, 176, 177, 178, 184, 191, 196, 197

POLYSULFIDE COOKING

Technology Description:

Polysulfide cooking differs from conventional kraft cooking in the fact that the cooking liquor contains polysulfides. Polysulfide cooking and its benefits have been know for many years. It was not until early in the 1970's, however, when a practical concept was developed for the catalytic oxidation of white liquor that polysulfide cooking liquor could be produced economically and without adverse environmental effects. Prior to this time, polysulfides were produced by injection of sulfite into the white liquor which resulted in an increase of sulfidity and increased air emissions. Two patented processes for catalytic oxidation of the white liquor are presently in use, one is the MOXY process developed by Mead Corporation and the second is a new process developed by Mitsubishi and the Chiyoda Corporation.[158,159]

Polysulfide cooking results in the ability to increase production yield at the same kappa number or to obtain the same yield at a lower kappa number. The major advantage of the process, however, lies in the fact that through its use less organic solids are produced in the black liquor resulting in a reduction in the load to the recovery boiler.[158] This decreased load has been reported as 100-200 pounds of organics/ton of production, or an average of 6%.[158] Use of this process can therefore more than offset the additional load imposed by oxygen delignification, which typically runs 2-4%.[8,158]

Polysulfide cooking is also compatible with anthraquinone cooking which is discussed in a subsequent section. Studies done at the Mitsubishi Shirakawa mill where both process are employed showed that the two process are synergistic.[158]

Effectiveness:

The effectiveness of polysulfide cooking is directly tied to those for oxygen delignification. Use of polysulfide cooking provides a means for mills that are recovery boiler limited to install oxygen delignification without the purchase and installation of a new recovery boiler.

Installations:

This process is presently in use at six mills which are listed in **Table V-8.**

Implementation:

The time required for installation from the date of order until start-up is reported to be 12 months.[159]

Costs:

The capital cost for installation of polysulfide cooking is reported to be $1.28, $1.85 and $2.23 million for a 500, 750 and 1,000 ADT/day mill, respectively.[158] The incremental operation costs for the same sized mills are reported to be $436,000, $642,000 and $822,000, respectively.[158] Based on the increased production resulting from

TABLE V-8

WORLDWIDE POLYSULFIDE COOKING REFERENCE LIST[159]

COMPANY	LOCATION	START-UP DATE
M. Peterson & Sons	Moss, Norway	1976
Sanyo-Kokusaku Pulp Company	Yufutsu, Japan	1979
Hyogo Pulp Kogyo KK	Tanigawa, Japan	1980
Zellstoff und Papierfabrik Frantschach AG	St. Gertraud, Austria	1981
Mitsubishi Paper Mills LTD	Shirakawa, Japan	1987
Mitsubishi Paper Mills LTD	Hachinohe, Japan	1990

polysulfide cooking and the earnings associated with that production, the simple return on investment (ROI) for the three alternatives is 7.2, 6.9 and 6.2 months, respectively.[158] These operating costs and ROIs would be even less according to the reference if polysulfide cooking were installed along with oxygen delignification.[158]

References:

158, 159

IMPROVED PULP WASHING

Technology Description:

The final stages of kraft pulping include a series of pulp screening and washing operations to remove black liquor (spent pulping liquor) from the pulp prior to bleaching. The efficiency of the final washing stages is particularly important with respect to consumption of chlorine in the bleach plant and formation of unwanted chlorinated compounds. Excess black liquor increases the chlorine demand of the brownstock pulp and sends excess lignin and associated breakdown products to the bleach plant. These lignin breakdown products have been proposed by one researcher as precursors to the dioxins and furans found in chlorinated pulps.[108]

Within the past decade there has been much improvement made in the area of brownstock washing. Many equipment options are now available including numerous pressure washers and pulp presses. The pressure washers operate at feed consistencies ranging from 2-4%, are generally more compact in size, require less space for installation and result in reduced effluent flows and energy savings.[29,121]. In addition to new technologies for the washing of brownstock pulp, computer optimization programs are now available to assist operators in the selection of washers.[98]

Effectiveness:

Not only do pressure washers results in reduced effluent flows and energy savings but studies have shown that the amount of organic contaminants carried over to the bleach plant is decreased when the consistency of the pulp is increased.[85] Computer simulation studies have shown that with good washing, the carryover to the bleach plant should be less than 10 kg/adt of COD and 5 to 8 kg/adt of dissolved solids measured as Na_2SO_4.[121]

Recent laboratory studies have shown that poor brownstock washing leads to increased levels of PCDDs and PCDFs in softwood pulps.[108] Results of these studies are shown in Table V-9.

TABLE V-9

THE EFFECT OF BROWNSTOCK WASHING ON THE FORMATION OF 2378-TCDD IN PULPS[108]

	2378-TCDD (ppt)	
	POOR WASHING	GOOD WASHING
C-Stage Pulp	7.3	3.3
E-Stage Pulp	6.3	2.1
D1-Stage Pulp	8.1	2.5
D2-Stage Pulp	9.3	ND(4.2)

During these studies the carryover of organics as measured by permanganate demand was 30% higher during poor washing. In addition to these results, it was found that use of surfactants during brownstock washing reduced the levels of PCDDs and PCDFs in the chlorinated pulp by 20-25% and that additional washing of the pulp prior to chlorination with large amounts of 50% aqueous ethanol reduced the amount of chlorinated dioxins and furans in the chlorinated pulp by 80%.[108]

Implementation:

Optimizing operation of existing washers can be accomplished in the short term (one to two months), subject to possible delivery of replacement parts. Installation of replacement washers or new washing systems may require several months to well over one year depending upon the scope of the project and equipment delivery. The new generation pressure washers, however are smaller, require less space because they require no drop leg and come as an assembled package, all of which should facilitate installation.

Costs:

Optimizing existing washing systems should require only minimal costs, and possibly could result in cost savings through decreased use of bleach plant chemicals. Costs for new or replacement pressure washing systems were estimated by one supplier to range from approximately $1 million for the smallest size to $1.8 million for the largest size.[112] The energy savings associated with pressure washers over drum washers were estimated by one source to be $104,000/year based on 3.2¢/kwH, and 100-130 pounds of steam/ton of pulp by another.[115,146]

References:

8, 29, 51, 85, 98, 108, 112, 115, 121, 141, 146, 192, 196

EMERGING TECHNOLOGIES

PRETREATMENT WITH NITROGEN DIOXIDE

Technology Description:

PRENOX® is a proprietary pulp pretreatment process developed by Olaf Samuelson and co-workers at the Chalmers Institute of Technology in Sweden.[10] The patent for this process is presently held by Sunds Defibrator AB, Sundsvall, Sweden. The process consists of pretreatment of kraft pulp under acidic conditions with one to two percent nitrogen dioxide (NO_2) at medium to high consistency and moderate temperatures.[9,10] This pretreatment is normally carried out after digestion and before oxygen delignification. Duration of NO_2 pretreatment ranged from 15 minutes to 120 minutes in pilot plant studies.[10] This technology allows up to 80% lignin removal in the oxygen stage which is normally limited to 50% by selectivity considerations.[31]

Effectiveness:

This pretreatment process has been extensively studied in the laboratory.[31] The laboratory results prompted four Swedish companies (AGA, Mo och Domsjo, Nobel Industries and Sunds Defibrator) to mutually finance a pilot plant which was built at the SCA mill in Ostrand.[10,36] Pilot studies have shown that delignification of 70 to 80% is possible which corresponds to a kappa number of nine to ten being achieved on softwood.[54,95] More recent studies by Samuelson have shown that kappa numbers below five can be achieved.[165] When followed by an oxygen bleaching stage, this technology has demonstrated high potential to reduce TOCL from the paper making process.[9,10,22,31,42,55] A pilot plant study demonstrated that TOCL loads can be reduced from approximately 6 kg per metric ton to 2 kg per metric ton for conventional bleach plants.[22] When compared to conventional oxygen delignification to kappa number 17, this pretreatment decreases the active chlorine required for 90% ISO brightness by 55%.[42] BOD_7, COD and total organic chlorine (TOCL) decrease 55%, and color decreases 75%.[42]

Pretreatment with nitrogen followed by oxygen delignification results in kappa numbers below ten for softwood. A combination of these processes followed by high chlorine dioxide(90%) resulted in TOCl values of less than 0.5 kg/ton of pulp.[54] This is a significant step toward the effluent limitation established by the Swedish government of 0.1 kg/ton to be achieved by the year 2010.

PRENOX also has an impact on aquatic toxicity of the wastewater effluent. Studies reported by Norden showed that when untreated PRENOX waste was tested that it showed lower aquatic toxicity for all species tested except MICROTOX. However, after biological treatment the toxicity was lower for all organisms when compared to unbleached and oxygen delignified pulps.[195]

The influence of PRENOX on chemical costs as well as on the quality of the effluent from a bleached kraft pulp mill were presented by Norden and are shown in **Table V-10.**

TABLE V-10

THE IMPACT OF PRENOX ON CHEMICAL COSTS AND EFFLUENTS[95]

	UNBLEACHED		O_2-DELIGNIFIED		PRENOX-O_2
Kappa Number	28		18		10
ClO_2 Substitution in 1st Stage	10	50	40	50	50
Chemical Cost, SEK[b]/t	187	217	176	179	164
COD, kg/t	75		49		22
AOX, kg/t	5.3	3.7	2.3	2.0	1.4

Chemical Prices:	Cl_2	1.20 SEK/kg
	ClO_2	2.60 SEK/kg
	O_2	0.70 SEK/kg
	NaOH	1.40 SEK/kg

Installations:

At the present time there are no mills employing this technology, however, Sunds Defibrator AB is currently looking for a Swedish mill at which to install a full scale demonstration facility. Two mills in Sweden have recently installed two stage oxygen delignification systems to facilitate conversion to PRENOX at some future date if the technology proves to result in lower AOX levels in the discharge then can be achieved with a two stage OD system.

Implementation:

Some of the concerns raised by the industry in Sweden relative to PRENOX are related to air emissions of NO_X and chemical availability. A trial burn done at the Norrsundet mill in Sweden showed that about five percent of the nitrogen added to the recovery boiler would be emitted as NO_X.[95,195] This calculates to an increase in NO_X emissions by about 0.5 kilogram per ton of production.[95] While it is unknown what problems exist with regard to chemical availability in the U.S., the usual source of supply in Sweden for the NO_2 was from fertilizer manufacturers. Even through the pilot plant studies showed that there were no problems associated with regard to the above concerns, industry remains skeptical and would like a full scale demonstration before proceeding.

The equipment required for PRENOX is similar to that for oxygen delignification. This being the case, the time for implementation should be similar to that required for oxygen delignification, two to three years.

Costs:

No cost information was found in the literature, however, capital costs should be similar to that for oxygen delignification systems as discussed in a previous section of this report.

References:

9, 10, 21, 22, 31, 36, 42, 54, 55, 95, 96, 165, 170, 173, 195

DEMETHYLATION

Technology Description:

Demethylation is a pulp pretreatment process that enhances delignification with peroxide and oxygen by creating additional reaction sites in the pulp where delignification occurs. Demethylation of pulp is accomplished using potassium thiophenoxide in diethylene glycol at 200°C.[42]

Effectiveness:

Laboratory studies have shown that demethylation followed by peroxide delignification can achieve a kappa number of 7.5.[42] This kappa number is typical of pulps entering the brightening stage. By enhancing pre-chlorination delignification processes, chlorine consumption theoretically should be reduced, resulting in less formation of TOCl.

Installations:

At the present date there are no facilities utilizing this technology.

Implementation:

Due to the relatively severe conditions required for demethylation, a practical process for full scale application has not yet been developed.[42] No data was found discussing implementability.

Costs:

No data is available, due to the experimental nature of the process.

References:

42, 59

ANTHRAQUINONE CATALYSIS

Technology Description:

Anthraquinone (AQ) catalysis is a process modification in the cooking phase, involving addition of anthraquinone to the alkali in a kraft cook. Anthraquinone is produced from coal tar from the coking process at steel mills. Through the addition of anthraquinone the pulping process is accelerated, and the amount of lignin in the resulting unbleached pulp is reduced.[78]

Effectiveness:

AQ catalysis has been well demonstrated in laboratory and pilot tests. The additional reduction of lignin prior to bleaching lowers chlorine consumption, thus reducing formation of TOCl. BOD and color in the mill effluent are also reduced.[69]

Installations:

Anthraquinone pulping is used at the Mitsubishi mill in Shirakawa, Japan.[158]

Implementation:

Anthraquinone pulping results in higher production costs, however, as pollution control costs escalate cost effectiveness will improve. The required rate of addition of AQ is fairly small (approximately 1 lb/ton of pulp) and does not require extensive process equipment modifications.[69] Although pulp viscosity is reduced somewhat, overall, pulp quality is similar to conventional cooking. Increased pulp yield of two to three percent has been reported.[78]

Costs:

Addition of AQ catalysis to an existing mill requires minimal capital investment. Increased operating costs, however, are not completely offset by reductions in bleaching chemical usage.[69]

References:

69, 78, 158

OZONE DELIGNIFICATION

Technology Description:

Ozone delignification is the use of ozone (O_3) in alkaline conditions, to delignify pulp. This technology like oxygen or peroxide delignification would occur before the chlorine stage of bleaching such that the waste liquor could be removed from the process and disposed of in the recovery system.

Effectiveness:

The available literature does not discuss TOCl analysis but one reference states that acidification of pulp followed by ozone treatment decreases kappa number of softwood pulps by 43% and of hardwood pulps by 47%.[38] This degree of delignification is similar to that obtained by oxygen delignification.

Installations:

At this time, the process is not commercially available and there are no known full scale installations.

Implementation:

A 1986 article reported that ozone delignification was operating at a pilot plant scale only.[38] The available literature discussing ozone delignification and associated pulp qualities appears contradictory. Reports range from stating that development of ozone bleaching has been hampered by the poor selectivity and resulting carbohydrate degradation and low yield and viscosity, to stating that O_3 and O_2 delignification have developed the same yield, final brightness and strength.[38,64]

Costs:

Based on limited information, this technology is more expensive than oxygen or peroxide delignification and does not result in any better pulp qualities than oxygen delignification.[38,42,64]

References:

34, 38, 42, 53, 54, 64, 73, 188

PEROXIDE DELIGNIFICATION

Technology Description:

Peroxide delignification is applying hydrogen peroxide in an alkaline medium prior to the chlorine stage of bleaching. Application of this principle is also covered under a separate section titled Peroxide Extraction. The discussion in this section is primarily directed toward the patented MINOX process. This process involves mild delignification of the brown stock pulp with hydrogen peroxide, high efficiency washing of the treated stock and recycling of the peroxide effluent to the brown stock washer unit. Chemical application is after brown stock washing.

Effectiveness:

Peroxide delignification studies carried out on different types of pulps showed that 22-29% delignification could be achieved on kraft hardwood, 25-42% on kraft softwood and 35-42% on sodium bisulfite hardwood.[154] Operating data from the Cellulose des Ardennes mill show that even for a mild delignification process, where the kappa number of the brownstock hardwood pulp is reduced from 17 to 14.4, that the color of the effluent was reduced by 45%.[154] Previously reported studies showed that peroxide delignification efficiency could be increased 40-60% by demethylation of the pulp.[42]

Installations:

The MINOX process has been used for many years on unbleached sulfite pulps and in late 1979 it was implemented on kraft pulp at the Cellulose des Ardennes mill in Harnoncourt, Belgium.[154]

Implementation:

One article states that E_{OP} can be used efficiently as a first bleaching stage in sulfite pulp mills but that due to the high content of heavy metal ions in kraft pulp brownstock it cannot be used for kraft pulp bleaching without an additional stage for eliminating heavy metal ions.[79] Information related to the operation of the Cellulose des Ardennes facility and research by PAPRICAN did not discuss any problems associated with heavy metal ions.[149]

Costs:

Capital cost data was not found in the literature, however, costs should be similar to those for oxygen delignification as the basic equipment needed is similar. One major difference would be in the retention tower which for peroxide delignification is approximately two hours as compared to oxygen delignification where the retention is 30 to 60 minutes. For retrofit situations, one author suggests that the P stage could be carried out in the high density storage tower and post bleaching could be reduced to three or four stages to reduce capital cost.[154] Costs reported for the one operating facility showed a savings of 1.1 $/ADT of pulp in direct operation costs.[154]

References:

42, 79, 149, 154

VI. MINIMIZATION OF CONTAMINATION THROUGH PROCESS CHANGES - BLEACHING

AVAILABLE TECHNOLOGIES

CHLORINE DIOXIDE SUBSTITUTION

Technology Description:

Chlorine dioxide (ClO_2) substitution is the replacement for some portion or, in some cases, all of the chlorine gas (Cl_2) used in the first bleaching stage for delignification. Chlorine dioxide is a more powerful oxidizing agent than chlorine, providing about 2.63 times the oxidizing power of an equivalent amount of chlorine. The amount of substitution or replacement is expressed as a percent of the total equivalent chlorine used and high substitution is loosely defined as 25 percent or greater.[103]

Chlorine dioxide must be produced and consumed on-site as it is unstable and not suitable for long-term transportation or storage. There are six commercial ClO_2 generators on the market today.[100] Each is operated with a reducing agent (SO_2, methanol, chloride ion from NaCl, or HCl), to form ClO_2 and various by-products ranging from chlorine, sodium sulfate and acid effluents. Selection of a particular generating unit is mill-specific and may be influenced by a number of process-related factors, most concerning consumption of residuals from the process

Chlorine dioxide has been used for pulp bleaching since 1946. In the 1960's the CEHDED and CEDED sequences became dominant for producing full bleach kraft pulp. In the 1970's attention was given to replacing part of the elemental chlorine in the first bleaching stage with equivalent chlorine dioxide to improve strength and color stability and reduce effluent color.[78] The use of ClO_2 has been steadily increasing as shown in **Figure VI-1**. Worldwide production of pulp bleached with high chlorine dioxide substitution is estimated to have reached 6.9 million tons/year by the end of 1988.[103] The degree of chlorine dioxide substitution at U.S. kraft pulp and paper mills as of mid-1988 is presented in **Table VI-1**.

During the past two years, the pulp industry has been increasing ClO_2 substitution at a relatively rapid rate. Pryke lists the following reasons for this increase:[103]

- Lower bleach plant chemical consumption
- Lower bleach plant costs
- Improve effluent quality (color, toxicity)
- Reduced formation of chlorinated organics (AOX,TOX, TOCl)
  Reduced formation of 2378-TCDD and 2378-TCDF

Various substitution methods are used in the industry and described in the literature. The two most common methods are sequential (DC or CD dependent on which is added first) and mixed (D+C). Studies have shown that

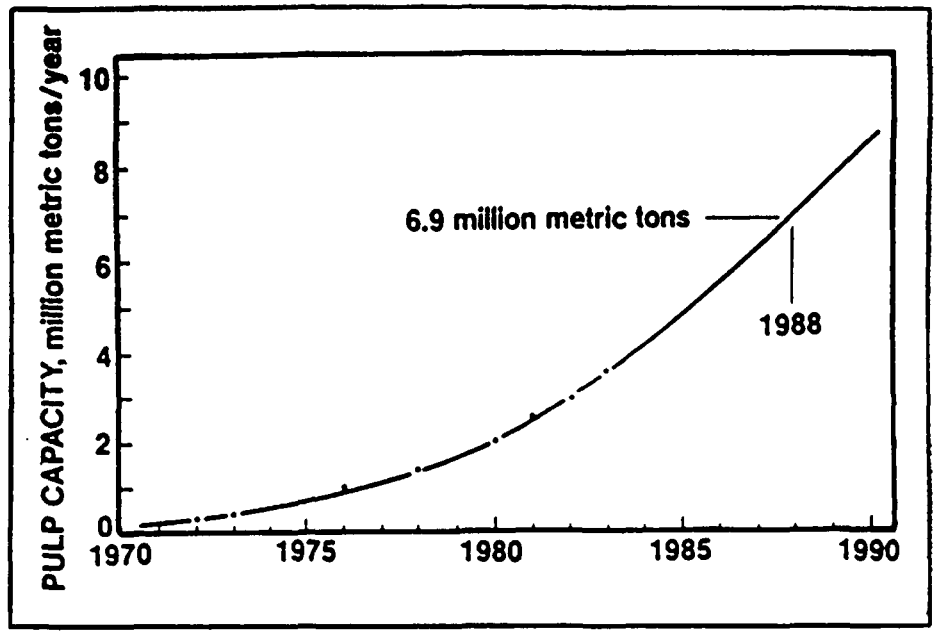

FIGURE VI-1 CHLORINE DIOXIDE IN THE CHLORINATION STAGE[103]

TABLE VI-1

CHLORINE DIOXIDE SUBSTITUTION
AT U.S. KRAFT MILLS (MID 1988)[163]

Percent Substitution	Number of Kraft Bleach Lines
0%	59
<5	16
5 - 10	41
10 - 20	33
20 - 30	9
30 - 40	1
40 - 50	3
>50	3
TOTAL	165

improved delignification is obtained by sequential addition with chlorine dioxide added first (DC).[103] The DC mode also generates less chlorate.[22,26] Emphasis here will be to discuss chlorine dioxide substitution in general.

Effectiveness:

Numerous studies have shown the influence of chlorine dioxide substitution on the formation and discharge of chlorinated organics.[22,26,59] As shown in **Figure VI-2,** increasing the substitution of ClO_2 up to 50% results in an increase in total chlorinated phenolics both for conventional and oxygen delignified kraft pulps. Beyond 50% substitution, however, the total amount of chlorinated phenolics decreases at a rapid rate. The effect of chlorine dioxide substitution on the formation of individual chlorinated phenolics such as di-, tri, and tetra-chloroguaiacols have been studied and are reported in the literature.[19,103] Formation of 4,5-dichloroguaiacol was found to increase with increasing ClO_2 substitution to 50%, then decrease as ClO_2 substitution was increased. Formation of 3,4,5 trichloroguaiacol and 4,5,6 trichloroguaiacol and tetrachlorocatechol was found to decrease with increasing ClO_2 substitution.

The impact of ClO_2 substitution on the formation of AOX is shown in **Figure VI-3.** As can be seen, AOX decreases linearly with increasing chlorine dioxide substitution. This relationship is further displayed in **Table VI-2** which also shows that increasing ClO_2 substitution has little impact on the BOD discharged. Studies have also shown that increased ClO_2 substitution results in decreased color in the effluent.[103]

TABLE VI-2

AOX AND BOD5 FOR VARIOUS LEVELS OF CHLORINE DIOXIDE SUBSTITUTION[133]

	CHLORINE DIOXIDE SUBSTITUTION			
	10%	30%	40%	50%
AOX, kg/tonne				
E STAGE	3.52	3.36	3.13	2.37
UNTREATED EFFLUENT	3.42	-	-	2.31
PRIMARY EFFLUENT	2.6	-	-	2
AFTER 2.5 DAYS SECONDARY TREATMENT	1.45	-	-	1.22
TREATED EFFLUENT (6 DAYS DETENTION)	1.39	-	-	1.15
FINAL EFFLUENT BOD5, tons/day	2.2	1.8	1.7	2.1

The impact of chlorine dioxide substitution on the formation of 2378-TCDD and 2378-TCDF has been the subject of numerous studies in the past few years.[40,90,91,162] One study done at a mill which employs oxygen delignification showed that increasing the percent substitution of ClO_2 resulted in a decrease in the amount of 2378-TCDD and 2378-TCDF produced and discharged, see **Table VI-3.** Another source reported that by increasing the chlorine dioxide substitution from five to 50% reduced the discharge of CDDs and CDFs by over 50%.[162] Most of the studies pertaining to the impact of chlorine dioxide substitution relate to the reduction of the chlorine multiple. This subject is covered in more detail in a subsequent section of this report entitled Control of Chemical Dosage.

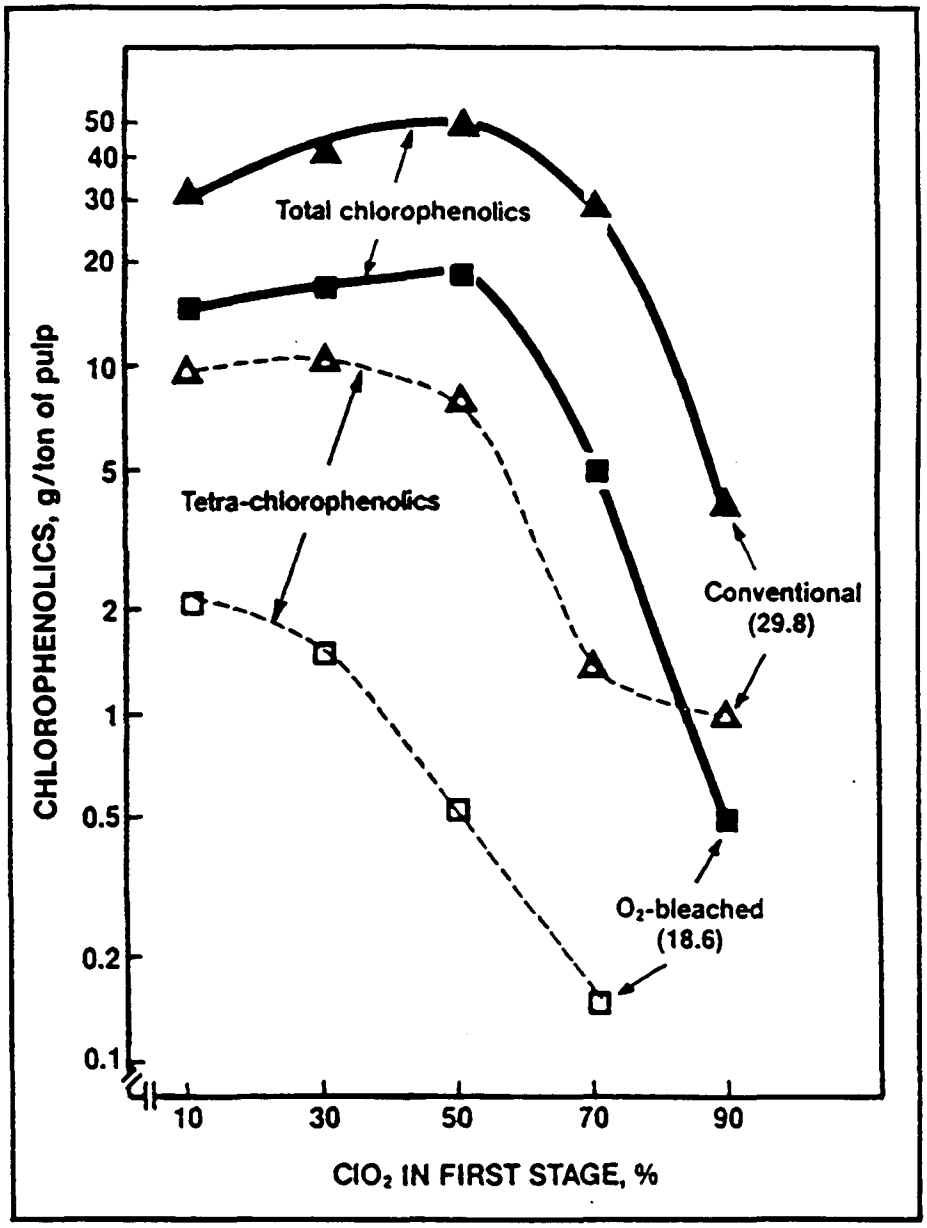

FIGURE VI-2 THE EFFECT OF CHLORINE DIOXIDE SUBSTITUTION ON TOTAL AND TETRACHLORINATED PHENOLIC COMPOUNDS[19]

Installations:

The number of U.S. bleach lines using ClO_2 and the percent substitution for mid 1988 are shown in Table VI-1. Since that time the number of mills employing ClO_2 and the percent substitution has increased. In the June 1987 issue of *Pulp & Paper*, the editor reported that In Canada nearly 90% of all bleach lines use more than 10% ClO_2 in the C-stage.[16]

Implementation:

Some of the more positive effects reported as a result of applying a large quantity of ClO_2 substitution (50% or greater) when compared to 0 to 15% ClO_2 substitution include: (a) no significant difference to improved pulp viscosity and strength;[26,38,68] (b) decreased sodium hydroxide consumption;[38,42,68] (c) higher yield.[68] Other

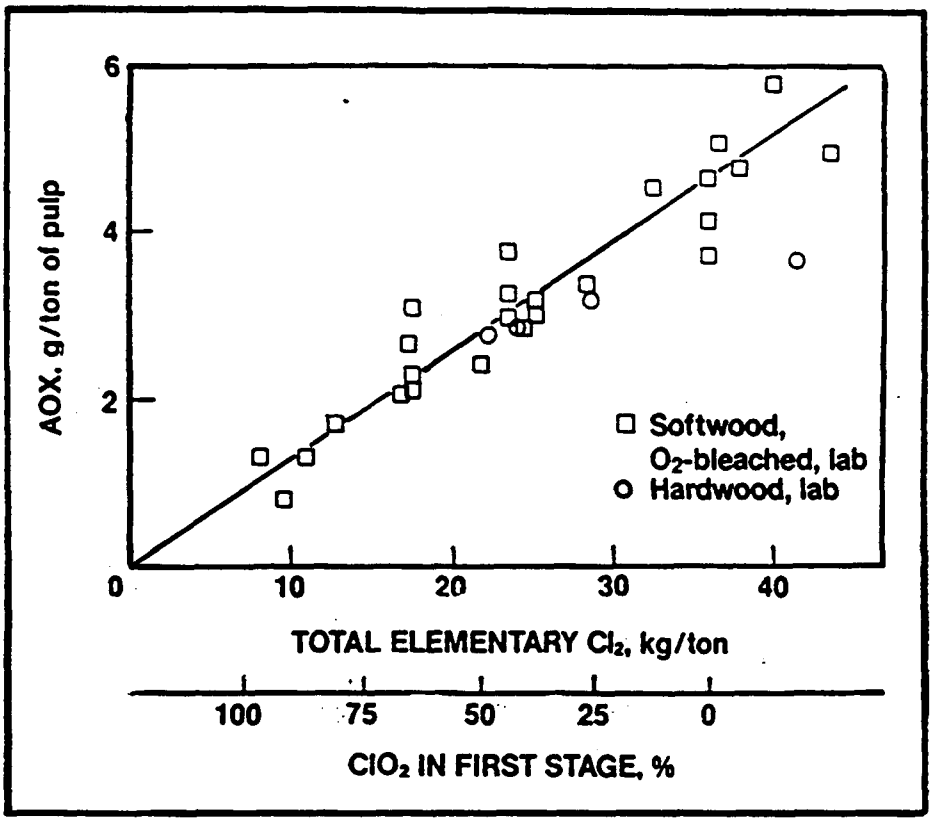

FIGURE VI-3 THE EFFECT OF CHLORINE DIOXIDE SUBSTITUTION ON THE FORMATION OF AOX[19]

TABLE VI-3

DIOXIN AND FURAN RESULTS FOR VARIOUS LEVELS OF CHLORINE DIOXIDE SUBSTITUTION[133]

	CHLORINE DIOXIDE SUBSTITUTION			
	10%	30%	40%	50%
C-FILTRATE 2378-TCDD, ppq	ND	ND	ND	ND
C-FILTRATE 2378-TCDF, ppq	ND	ND	ND	120
E-FILTRATE 2378-TCDD, ppq	170	65	190	ND
E-FILTRATE 2378-TCDF, ppq	490	320	1,000	470
TOTAL UNTREATED EFF. 2378-TCDD, ppq	ND	ND	NOT TESTED	ND
TOTAL UNTREATED EFF. 2378-TCDF, ppq	63	52	NOT TESTED	ND
SECONDARY EFFLUENT 2378-TCDD, ppq	ND	NOT TESTED	NOT TESTED	ND
SECONDARY EFFLUENT 2378-TCDF, ppq	45	NOT TESTED	NOT TESTED	ND

advantages claimed from use of chlorine dioxide include higher final brightness and better brightness stability (percent substitution not specified in article).[78]

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Some of the negative effects of increased ClO_2 substitution reported in the literature include: (a) oxygen bleached pulp is delignified by ClO_2 considerably more slowly than non-oxygen bleached pulp. $C10_2$ and oxygen both favor reaction with lignin containing free phenolic groups. Oxygen delignification specifically attacks such lignin, therefore reducing the amount of free phenolic groups to react with ClO_2.[59] Thus a bleaching sequence incorporating oxygen delignification followed by high ClO_2 substitution, the time required for bleaching may be increased; (b) increased use of ClO_2 will result in more salt cake by-product from ClO_2 generation. This additional salt cake may exceed that which is required for kraft mill make-up;[69] (c) in laboratory tests, carbon monoxide (CO) was observed during ClO_2 bleaching of hardwood and softwood pulps. The amount of CO generated depends on the lignin content of the incoming pulp (greater lignin yields more CO) and the charge of the ClO_2 (a higher charge yields more CO) and (d) significant amounts of chlorates are formed during bleaching with ClO2. In Sweden discharge of high levels of chlorates was found to have a negative effect on ecologically important macroalgea (e.g. *Fucus vesiculosus*).[22] Biological treatment has been found to reduce these chlorates by 80%.[180]

Increasing ClO_2 substitution within the generating capacity of an existing on-site ClO_2 generator should be a relatively short term project, and probably has been accomplished at most U.S. mills. However, as shown in **Table IV-1**, presented earlier, few mills in the U.S. practice ClO_2 substitution at the high rates noted above as necessary to affect minimum formation of chlorinated organics. Currently there are numerous projects underway for increasing chlorine dioxide substitution at bleached kraft mills such that delivery times for ClO_2 generating equipment have increased. Implementation time for these new large-scale ClO_2 generating systems is probably now more affected by equipment delivery than by engineering design or construction. One source gave an implementation time from date of order to operation as 14-18 months.[190] Another factor may be the availability of sodium chlorate which according to a bleaching survey reported in June 1988 was in short supply.[4]

Costs:

The capital cost for a 30 ton/day system was provided by one source as approximately $2.8 million for equipment with an installed cost of approximately $5.7 million.[190] Data from five mill trials reported by Pryke and shown in **Table VI-4** show that bleach plant chemical costs are reduced with substantial chlorine dioxide substitution.

TABLE VI-4

MILL TRIAL CHANGES IN BLEACHING CHEMICAL CONSUMPTION AND COSTS[103]

	Mill A	Mill B	Mill C	Mill D	Mill E
Increase in ClO_2 substitution, %	14 to 45	17 to 35	10 to 30	10 to 30	4 to 26
Total equiv. Cl_2, % on pulp	-0.74	-0.60	-0.95	-0.76	-0.74
Total applied NaOH, % on pulp	-1.00	-0.45	-0.45	-0.68	-0.38
Bleaching cost, CDN$/a.d.ton	-1.94	-1.55	-2.36	-3.20	-1.40

Bleaching costs were calculated using CDN$0.265/kg of Cl_2, CDN$0.265/kg of NaOH, and CDN$1.10/kg of ClO_2

References:

4, 16, 18, 19, 20, 22, 26, 30, 33, 38, 40, 42, 44, 46, 47, 54, 58, 59, 62, 68, 69, 71, 73, 78, 85, 90, 91, 93, 95, 100, 103, 105, 109, 118, 121, 133, 143, 144, 149, 150, 162, 163, 166, 170, 172, 173, 178, 183, 185, 186, 188, 190, 199

OXYGEN EXTRACTION

Technology Description:

In conventional bleaching, an acidic chlorination stage followed by an alkaline extraction stage constitute the first two bleaching stages. Adding elemental oxygen to the first extraction stage (E1) reduces the need for subsequent chlorine bleaching chemicals. Oxygen extraction can also be used prior to chlorination especially if combined with peroxides as described in the next section.[43,79,149,174]

Effectiveness:

When replacing the E1-stage with an E_O-stage in the (DC)EDED or (DC)ED sequence, pollution load can be reduced by 25 to 30%.[38] Whereas BOD and COD are both reduced through use of oxygen extraction, oxygen delignification and ClO_2 substitution are pointed out as being superior to E_O in reducing pollution.[22,69] TOCl reduction resulting from installation of an oxygen extraction (E_O) stage is not discussed in the literature, but other parameters discussed indicate pollution reduction and possible reduction in TOCl. Three out of four articles stated that E_O reduces ClO_2 and/or hypochlorite (H) consumption in kraft pulping, but no comparison was made showing TOCl reduction with associated reduction in ClO_2 and/or H use.[38,42,61,69] As a possible indicator, one article reports that with 70% ClO_2 substitution in the C-stage, a chloroform concentration of 0 µg/g of oven dry pulp was measured in the effluent filtrate.[18] In the same study, the H stage generated 5 to 15 times as much chloroform as the C, E and D stages combined. The article also stated that chloroform production from the D stage has been shown to be minimal. With this in mind, E_O followed by D stages would be expected to have minimal effect at reducing chloroform whereas E_O followed by a hypochlorite stage would reduce chloroform formation by reducing hypochlorite consumption. At one facility, installation of oxygen extraction improved bleaching by reducing kappa number after the CE sequence from 5.3 to less than 4.0 and the mill reduced hypochlorite use by 20 lb/ton.[50]

Installations:

By the end of 1984, over 55 E_O-stages (use of oxygen in the first alkaline extraction stage of chemical pulp bleaching) were in operation.[41] As of June 1987, in Canada, 80% of all bleach lines use oxygen extraction.[16]

Implementation:

In 1983, an oxygen extraction unit was installed at a 450 tpd bleach plant (softwood and hardwood) having an original CEHH sequence. Construction of the project was completed in three months.[50]

The only potential problems identified in the literature were: (a) oxygen channelizing in towers leading to non-homogeneous bleaching; and (b) the possibility of hazardous concentrations of hydrocarbons and carbon monoxide in dead zones within the bleaching tower or bleaching building. [61]

Costs:

The only capital cost information found discussed the 1983 oxygen extraction unit installation. The cost for the installation was under $500,000. The same project reported capital costs being repaid after the first year of operation due to hypochlorite savings. Use of oxygen extraction was reported by one company as resulting in a hypo savings of 8.3 pounds/ADT a caustic savings of 12 pounds/ADT and a steam savings of 200 pounds/ADT resulting in an approximate annual savings of $400,000 and a payout before taxed of 1.3 years.[200] Another article reported "phenomenal" operational savings of $400,000 to 800,000 (Canadian) per annum per installation.[42] Other articles report reduced ClO_2 and hypochlorite usage without presenting associated cost savings or increases.[38,42,61] Article 42 states that for softwood pulps, savings of 6 kg/ton of hypochlorite and 2 kg/ton of ClO_2 can be achieved in a CDE_oHDED sequence and 4 kg/ton of ClO_2 in CDE_oDED sequence with four to eight kg/ton of O_2 applied. Use of oxygen extraction at the SCA Ostrand mill is reported to have saved 16 pounds of bleaching chemical as active chlorine per ton of pulp.[65]

References:

15, 16, 18, 19, 22, 28, 31, 38, 41, 42, 43, 48, 50, 57, 61, 65, 69, 70, 73, 79, 83, 93, 127, 133, 149, 171, 172, 173, 174, 187, 188, 200, 202

PEROXIDE EXTRACTION

Technology Description:

This technology is similar to oxygen extraction (E_O) in that a small percentage of hydrogen peroxide (H_2O_2) is added to the alkaline extraction stage (E_P). Like E_O, adding peroxide to the extraction stage also reduces the need for subsequent chlorine bleaching chemicals. Peroxide can also be added to or "reinforce" an E_O-stage (E_{OP}) to further reduce chlorine bleaching chemical usage.[79]

Effectiveness:

E_{OP} or E_P after chlorination can be used to reduce hypochlorite and ClO_2 in subsequent bleaching stages.[28,79] In a laboratory study,[22] (DC)E_P sequence (H_2O_2 of 0.2% per ton of pulp) reduced pulp kappa by 0.5 to 1.0 more than for the (DC)E sequence. The addition of 0.3 to 0.4% peroxide to the E_O-stage is reported to increase delignification from 10-15% for E_o alone to 30 to 35%.[4] This increase in delignification is directly proportional to a decrease in chlorine consumption which can be reduced from 20-35% through use of peroxide in the extraction stages.[194] No specific TOCl analyses were presented but bleach chemical use, primarily ClO_2 and hypochlorite will be reduced with the use of peroxide in the E_O-stage for kraft pulp. It has been reported that using 0.1% peroxide in the second extraction stage results in up to a 0.2% savings in chlorine dioxide which if used for substitution of chlorine in the first stage of bleaching could results in a 5 kg/tonne reduction in elemental chlorine.[194] At a minimum as with oxygen extraction (E_O), peroxide extraction (E_P) or peroxide reinforced extraction (E_{OP}) can reduce chlorate formation by reducing ClO_2 use. One article reported that the combining action of H_2O_2 with that of oxygen makes it possible to better control the oxygen-alkali extraction stage.

For sulfite mills, reinforcing on Eo stage with oxygen hydrogen peroxide (E_{OP}) and placing the E_{OP} as the first bleaching stage can reduce chlorine consumption. In one comparison of a CEHH and (E_{OP})CHH sequences, it was found that the (E_{OP})CHH process used less than one half the chlorine to bleach pulp to paper grade quality while bleaching costs of the two processes were approximately the same.[79]

Installations:

The June 1987 *Pulp & Paper* reported that in North America, 25% of the bleach lines use peroxide and that use of peroxide grew by 30% from 1983 to 1987.[16]

Implementation:

The only limitation discussed was that pH must be maintained around 10.5.[78]

Costs:

No costs were provided for kraft pulping. For sulfite mills, the operating costs for a CEHH and (E_{OP})CHH were reported to be about the same.[79] Capital costs were not discussed.

Costs need further investigation. One reference states that H_2O_2 is expensive for bleaching chemical pulps as compared to ClO_2 but that as energy costs increase, the cost differential between the two chemicals rapidly decreases.[78] Another reference states that the economics of adding H_2O_2 along with oxygen in the first extraction stage, depends on relative costs of various chemicals but that in most cases, operating costs would be noticeably decreased.[22] E_P-stage is financially less attractive than E_O.[28]

References:

15, 16, 22, 28, 38, 53, 54, 64, 73, 78, 79, 149, 167, 174, 188, 194, 195, 204, 206

MONOX-L PULP BLEACHING PROCESS

Technical Description:

Monox-L is hypochlorous acid (HClO) plus an additive developed and patented by Quantum Technologies. Hypochlorous acid (L), the hydrated form of chlorine monoxide, has been known of since the 1930s as an excellent bleach chemical, however, it has not been used as it is quite destructive of the pulp.[124] Quantum's developed additive maintains bleaching characteristics without pulp destruction.[124] In many ways, Monox-L can be compared to chlorine dioxide due to its bleaching condition and abilities. The process equipment metallurgy required for Monox-L is reported to be the same as that needed for chlorine dioxide.[124]

Effectiveness:

While Monox-L is generally used in place of chlorine dioxide it can be used to replace hypochlorite or hydrogen peroxide. This replacement is reported to produce, a superior pulp in terms of brightness, viscosity, and chloroform reductions.[25] Research results reported by Quantum Technologies indicate that although L bleached samples show some concentrations of chloroform present in the bleach filtrate (2.2 ppm), the quantity formed is much lower than for the corresponding H stage (5.4 ppm).[25] The L sample produced a pulp of higher brightness than the H sample and formed about 60% less chloroform.[25] A chlorine dioxide (ClO_2) bleached sample was also tested for chloroform formation. Although ClO_2 itself does not form chloroform, 1.7 ppm of chloroform was present in the D-stage filtrate which was most probably due to carry over from the previous bleaching stages.[25] By comparison, chloroform in the L-stage filtrate was 2.2 ppm which was only slightly higher than that formed during the chlorine dioxide bleaching.[25]

While Monox-L has may similarities to chlorine dioxide, it is claimed by Quantum to offer numerous advantages over chlorine dioxide such as lower energy requirements, lower capital and operational cost, less hazardous, and less space requirements.[124,135] In addition to using Monox-L as a substitute for chlorine dioxide, research by Quantum shows that when Monox-L is substituted for chlorine that the amount of AOX and dioxin is reduced in pulps and bleach plant filtrates.[130,135] The data are shown in **Table VI-5** and **Table VI-6.**

TABLE VI-5

AOX LEVELS IN FILTRATES FOR BLEACHED SCANDINAVIAN SOFTWOOD[130,135]

FIRST STAGE BLEACH CHEMICAL(S)	AOX, kg/ADT		
[5% ACTIVE CHLORINE]	C-STAGE	E-STAGE	TOTAL
C(90%) D(10%)	2.0	1.6	3.6
C(50%) D(50%)	1.42	1.38	2.8
L(100%)	1.03	1.13	2.26
L(50%) D(50%)	0.65	0.83	1.48
D(100%)	0.32	0.35	0.67

TABLE VI-6

C-STAGE SUBSTITUTION WITH MONOX-L[135]
(TOTAL ACTIVE CHLORINE - 7.4%)

BLEACH SEQUENCE	2378-TCDD, ppt PULP	2378-TCDD, ppt FILTRATE	2378-TCDF, ppt PULP	2378-TCDF, ppt FILTRATE
L E	-	ND	-	ND
L E H	ND	-	ND	-
L E H E D	ND	-	ND	-
C E	-	-	-	-
C E H	38	-	20	-
C E H E D	16	-	8	-

While these data do show a reduction in AOX and dioxin, there is no information about the quality of the final product. It is also interesting to note that while Monox-L substitution for chlorine results in lower AOX levels that substitution of chlorine dioxide results in an even greater reduction of AOX.

The substitution of Monox-L for chlorine dioxide in the D1 or D2 stages of bleaching would allow for that chlorine dioxide displaced to be substituted for chlorine in the chlorine stage. This would offer a means for mills with limited chlorine dioxide generation capacity to increase the amount of chlorine dioxide in the chlorine stage of bleaching.

Installations:

A commercial size 20 ton per day Monox-L generator has been operating at the Kymmene Corporation mill at Kuusankoski, Finland since February 1989.[124] This was the first commercial installation of the Monox-L technology and resulted from two successful plant trials conducted in early 1988 and late 1987.[124] Plant trials have been recently run at Federal Paper Board - Riegelwood, N.C., Georgia-Pacific Corporation - Brunswick, Georgia, and Temple-Inland, Inc. - Evadale, Texas.[124] Based on these trials, Georgia-Pacific and Temple-Inland have purchased a 25 and 20 ton per day Monox-L generator, respectively, with start ups anticipated in the first quarter of 1990.[135]

Implementation:

Quantum estimates the time required for design, installation and start-up to be approximately six months from the receipt of the purchase order, four months under expedited conditions, and nine months with approval delays.[135]

Costs:

The installed capital cost for a 20 ton per day Monox-L generator with prepaid license and royalty was recently quoted by Quantum to be approximately $2 million.[135,198] This cost can be compared to a comparably sized chlorine dioxide generator costing $6-12 million plus royalty.[135] The 25 ton per day unit and peripheral equipment at Kuusankoski is reported to have cost just under $2 million.[124] Operation and maintenance costs were quoted by Quantum at approximately $9 per ton for Monox-L as opposed to $170 per ton of chlorine dioxide.[135] When

comparing costs one should take into account the fact that Monox-L replaces chlorine dioxide at a ratio of approximately 1.2 pounds of Monox-L for 1.0 pound of chlorine dioxide.[135] Another reference states that the substitution of Monox-L for chlorine dioxide results in a savings of approximately $5/ton of pulp.[198]

References:

25, 124, 130, 135, 198

CONTROL OF CHEMICAL DOSAGE

Technology Description:

The chlorine ratio is the amount of equivalent chlorine, including that contributed by chlorine dioxide, consumed in the first pulp bleaching stage in relation to the lignin content of the incoming pulp, expressed as the kappa No. The chlorine ratio, also referred to as the chlorine multiple or kappa factor, is computed as follows:

Chlorine ratio = $[((Cl_2+2.63*ClO_2)/2000)*100]$/kappa No.,

where Cl_2 and ClO_2 are chemical application rates in lbs/ton of air-dried brownstock pulp.

Research conducted in Sweden has demonstrated that control of chlorination by monitoring the chlorine ratio can be effective for minimizing formation of 2378-TCDD and 2378-TCDF. Laboratory and mill scale trials indicate that formation of 2378-TCDD/TCDF is substantially reduced at chlorine ratios of 0.15 and less and increased at chlorine ratios of 0.20 and above. As of mid-1988, chlorine ratios for most U.S. bleach lines were found to be above 0.20.[163] Researchers report that overchlorination, even for brief periods of time can result in excess formation of 2378-TCDD/TCDF. Accordingly, chlorine minimization to achieve low chlorine ratios and close monitoring of chlorine application are necessary to affect control via chlorine ratio. For many U.S. bleach lines, the types of instrumentation and controls for chemical application rates are not advanced. Monitoring and control of chemical application rates to the degree necessary to control the process by chlorine ratio may not be possible without improved controls or close operator attention. Nonetheless, the research suggests that minimizing chlorine consumption and overchlorination will have beneficial impacts on reducing formation of 2378-TCDD/TCDF.

Effectiveness:

Laboratory experiments, confirmed by mill scale trials, demonstrate that control of the first bleaching stage by chlorine ratio was effective at substantially reducing formation of 2378-TCDD/TCDF. These results are shown in **Figure VI-4** and suggest that chlorine ratios below 0.15 are essential for minimizing formation of 2378-TCDD and 2378-TCDF.

Installations:

At this time it is not known how many mills are operating bleach plants to control the chlorine multiple at a level of 0.15 or less as a means to reduce the amount of dioxins and furans produced. Recent submissions by many of the 104 mills studied by EPA and the Paper industry indicate that efforts are being made by many mills to reduce their chlorine multiple toward the 0.15 level.[163]

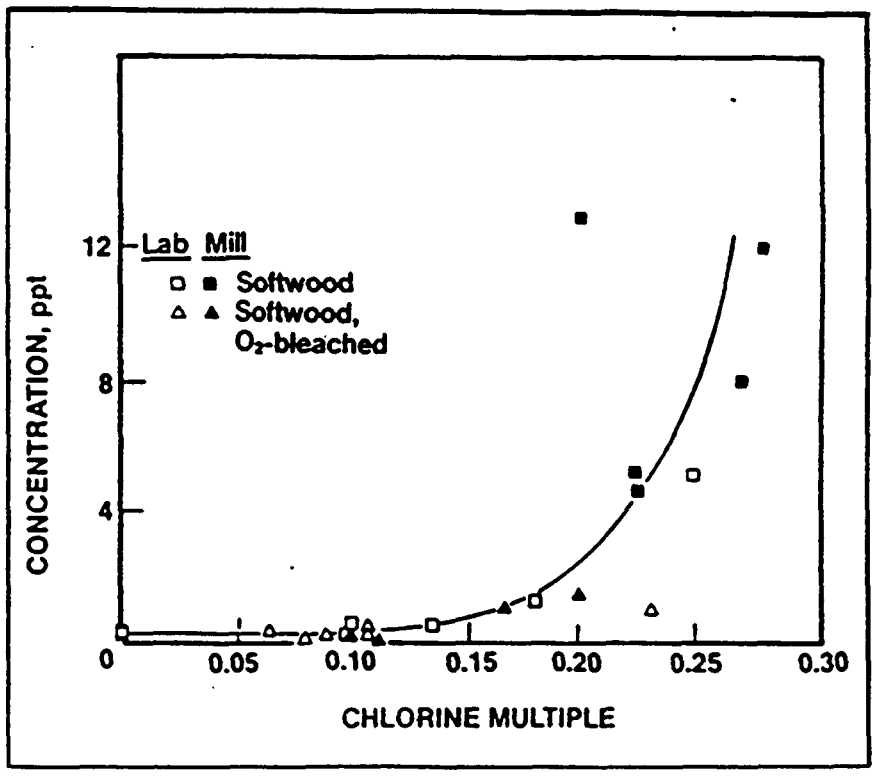

FIGURE VI-4 THE EFFECT OF CHLORINE MULTIPLE ON 2378-TCDD IN PULP[19]

Implementation:

Implementation time for minimizing chlorine consumption and overchlorination in the first bleaching stage within the capability of existing instrumentation and monitoring equipment at a mill should be a relatively short term project, perhaps taking a few months. Retrofitting more sophisticated controls on existing bleach lines to more closely continuously control chemical application rates may take several months or longer, depending upon availability and delivery of equipment. Additional research is necessary to determine the current state of the market.

Costs:

Costs for minimizing chemical applications at existing bleach lines should be minimal, exclusive of new instrumentation and controls. Costs for new systems are highly site-specific. Generalized costs are not available at this writing.

References:

13, 17, 19, 23, 26, 30, 33, 40, 85, 90, 91, 93, 103, 105, 118, 141, 149, 183

IMPROVED MIXING

Technology Description:

Effective chlorination stage mixing is important to reduce bleaching costs through more effective use of chemicals, to reduce downstream equipment requirements for new bleach plants, and to minimize formation of chlorinated organic compounds in bleached pulps and bleach plant process wastewaters. Prior to the early 1980's, most in-line mixers in use for chlorine addition were of the static design. Recently, high intensity mixers have become more popular for the reasons set out above. With the strong trend toward increased chlorine dioxide substitution for chlorine, additional mixers are necessary as ClO_2 is usually applied upstream of chlorine addition for maximum benefit. Thus, at many mills, reconfiguration of the mixing systems and chlorination stages has occurred or is underway to accommodate increased ClO_2 substitution. In most cases, combinations of various types of mixers are used to attain desired results.

Effectiveness:

Although little published data are available that specifically address the effectiveness of improved mixing on formation of chlorinated organics, several researchers have cited high efficiency chemical mixing and sequential or multi-step chlorine additions as important variables in that regard.[52] High efficiency mixing has also been cited as an important factor to minimize localized overchlorination and thus formation of 2378-TCDD/TCDF.

Implementation:

No information on implementation time is available at this writing, although, depending upon the system design and extent of bleach plant modifications, implementation times of several months to more than one year would appear reasonable.

Costs:

A new high shear mixer recently installed at one location was reported to have cost $160,000.[134]

References:

41, 42, 46, 47, 50, 52, 90, 104, 115

SPLIT CHLORINE ADDITION AND pH ADJUSTMENT

Technology Description:

The technology consists of process modifications which allow for chlorine/chlorine dioxide to be added in several small sequential charges rather than in a single charge and modifications which allow the pH of the chlorine stage be controlled to higher levels than conventionally practiced. Research at Westvaco showed that the rates of formation of 2378-TCDD and 2378-TCDF are more dependent on the concentration of the chlorine than on the absolute amount of chlorine used, or on the ratio of chlorine to the kappa number.[52] By applying the chlorine in several charges throughout the reaction time, the chlorine concentration "profile" can be kept lower.[52] Chlorine reacts with the residual lignin in the pulp by oxidation and by substitution mechanisms. While oxidation leads to more soluble lignin products, substitution results in the creation of chlorinated organics including CDDs and CDFs. Numerous studies have been carried out in an attempt to distinguish between these two reactions or to determine how to manipulate bleaching conditions to favor oxidation. In addition to lowering the concentration of chlorine through smaller additions, the concentration can also be reduced by upward adjustment of the pH. This fact is well documented in the literature, however, is not usually practiced because such adjustment results in a degradation of cellulose as seen by a decrease in pulp viscosity. Westvaco has developed operating conditions that control this loss of viscosity.[52]

Effectiveness:

Laboratory studies performed by Westvaco showed that by splitting the chlorine charge into three smaller doses, 2378-TCDF and 2378-TCDD concentrations in the pulp were reduced by about 70% and 50%, respectively.[52] In conjunction with the split chlorine charge, it was also found that by increasing the C-stage pH both 2378-TCDD and 2378-TCDF levels in the pulp were reduced by more than 90%.[52] Initial full scale mill trials have confirmed the capability to manufacture high-quality bleached products with nondetectable levels of 2378-TCDD and less than six parts per trillion of 2378-TCDF in the pulp.[52] The system has also been shown to be effective on both hardwood and softwood bleach lines with softwood showing the greatest response.[52]

The process changes modification were initiated at the Westvaco Luke mill in May 1989. CDD/CDF sampling and analysis performed both before and after these changes were initiated are presented in **Table VI-7.** During the period May 1989 through September 1989, only two of three planned addition points were in operation and during some months trial runs employing chlorine dioxide substitution and peroxide reinforcement were being performed. As can be seen from this table, the 2378-TCDD/TCDF levels have been reduced significantly in the pulp as well as in the effluent and sludge as a result of the changes made to date. The company is hopeful that when all the changes are completed and the additional chlorine dioxide substitution is on line that the levels of 2378-TCDD/TCDF will be even lower.[134]

TABLE V-7

WESTVACO (LUKE, MD) DIOXIN/FURAN ANALYSES

		BLEACH PLANT PULP				
		CHLORINATION STAGE		FINAL BLEACH STAGE		
DATE	SPECIES	2378-TCDD (ppt)	2378-TCDF (ppt)	2378-TCDD (ppt)	2378-TCDF (ppt)	SAMPLE TYPE[a]
9/87	Blend	43	124	36	143	24C/W
6/88	Blend	-	-	29	157	120C/R
12/88	Blend	4.0	18	2.6	20	MC/W
1/89	Blend	ND(4.4)	ND(41[b])	ND(1.0)	4.5	MC/W
2/89	Blend	-	-	4.4	10.2	MC/W
3/89	Blend	-	-	2.8	ND(8.0[b])	MC/W
4/89	Blend	-	-	ND(0.2)	ND(1.4[b])	MC/W
5/89	Blend	-	-	ND(0.2)	0.56	MC/W
5/89[c]	Blend	-	-	ND(0.2)	0.56	MC/W
6/89	Blend	-	-	ND(2.3)	ND(1.6)	MC/W
7/89	Blend	-	-	ND(0.1)	0.77	MC/W
8/89	Blend	-	-	ND(0.09)	0.8	MC/W
9/89	Blend	ND(0.05)	0.39	ND(0.06)	0.95	MC/W

	WASTEWATER TREATMENT PLANT						
	INFLUENT		EFFLUENT		SLUDGE		
DATE	2378 TCDD (ppq)	2378 TCDF (ppq)	2378 TCDD (ppq)	2378 TCDF (ppq)	2378 TCDD (ppt)	2378 TCDF (ppt)	SAMPLE TYPE[a]
9/87	40	350	ND(14)	101	47	524	24C/W
6/88	-	-	16	49	80	471	120C/R
12/88	ND(30[b])	151	ND(8)	58	13	56	MC/W
1/89			ND(13)	ND(26[b])	ND(10.3)	37	MC/W
2/89	-	-	9.0	17	7.2	24	MC/W
3/89	-	-	ND(10)	18	3.5	7.6	MC/W
4/89	-	-	ND(5)	20	4.6	17.4	MC/W
5/89	ND(8)	40	ND(8)	ND(5)	ND(0.24)	1.7	MC/W
5/89[c]	-	-	-	-	ND(0.44)	1.9	MC/W
6/89	-	-	ND(3)	ND(3)	ND(1.4)	1.9	MC/W
7/89	-	-	ND(1)	5	3.2	38.0	MC/W
8/89	-	-	ND(1)	4	0.6	4.6	MC/W
9/89	ND(3)	10	ND(1)	ND(4[b])	1.1	13.9	MC/W

[a] 24C/W - 24 hour composite/Westvaco
120C/R - 120 hour composite/Requested by Environmental Agency (104 Mill Study)
MC/W - Monthly composite/Westvaco

[b] Estimated maximum potential concentration

[c] Duplicate

Installations:

As of the present date, this technology developed by Westvaco, has been installed at all three of its bleached kraft mills. This includes two bleach lines at each of the Covington, Virginia and Luke Maryland mills and one bleach line at the Wickliffe, Kentucky mill.[134] No other installations are known of at this time.

Implementation:

Westvaco's goal in undertaking the research was to develop an operation for significantly reducing dioxin levels that could be implemented in a short period of time, would not require extensive capital and would not result in production downtime. The system consists of valves, piping, pumps and high shear mixers all of which are readily available and can be designed and installed in a short period of time. The total time that it took Westvaco, from the date of decision until operation, for its Luke and Covington mills on an expedited schedule was seven to eight months, whereas for the Wickliffe mill running on a more typical schedule, it was approximately 13 months.[134]

Costs:

Westvaco's dioxin control program for its three bleached kraft mills (Luke, MD; Wickliffe, KY; Covington, VA) which includes five bleach lines was reported to have a capital cost of 25 million dollars.[134] In addition to the split chlorine addition and pH control process changes, this total cost also includes additional ClO_2 generation equipment at all three mills.[134] Of the total 25 million total, ten million was spent at the Luke mill where the changes were added to two bleach lines and 16 tons/day of ClO_2 generation was added.[134]

References:

81, 82, 134

MONITORING OF KAPPA NUMBER

Technology Description:

On-line measurement of kappa number is now possible with an optical analyzer developed and patented by STFI (Swedish Pulp and Paper Research Institute) and called the STFI OPTI-Kappa analyzer®. The STFI method is based on the ultraviolet light adsorption by the lignin in the pulp. Results are obtained in approximately five minutes as compared to the laboratory method which takes about one hour. Correlation with the laboratory methods are reported as very good for all species and a wide kappa number range.[122] The ability to measure kappa number on-line means that mills through close control of bleach chemical dosages can control the chlorine multiple as a method of reducing the amount of dioxins and furans produced as discussed previously in this document.

Effectiveness:

Use of this technology not only allows for the control of the chlorine multiple but can result in a reduction in the variation in the kappa number and a general reduction in the kappa number with no loss of product quality. One reference reports that at one installation the variability in the kappa number was reduced by 50% and the target kappa number was decreased by one to two kappa number units without any change in pulp quality.[122] Both of these results in the ability to reduce the chemical bleach dosage with results in the decrease in production of chlorinated organics. Results from the Iggesund mill showed a decrease in residual chlorine by about 3 kg Cl_2/ton of pulp, which corresponds to a decrease in the charge of active chlorine by 6-8 kg/ton.[111] This is reported to not only result in reduced production cost but reduced environmental effects.[111]

Installations:

Installations of the STFI OPTI-Kappa Analyzer are provided in **Table VI-8.**

Implementation:

Delivery time for the STFI OPTI-Kappa Analyzer was provided by the supplier as running from 10 to 15 weeks.[151]

Costs:

The capital cost of the unit including sensor, one sampling point, and computer installed and calibrated is approximately $196,000.[151] Each unit will handle up to three sampling point with each additional sampling point costing approximately $20,000.[151] ABB Industrial Systems Inc. who market the STFI OPTI-Kappa analyzer in North America, claim that the capital cost of the analyzer can be paid back is less than one year from the chemicals saved in the bleach plant. These annual chemical savings were reported by one author as SEK 1.5 million.[122] Another reference stated that bleach costs were decreased $2.4 per ton of pulp.[111]

References:

111, 122, 151

TABLE VI-8

WORLDWIDE STFI OPTI-KAPPA® INSTALLATIONS REFERENCE LIST[a]

CUSTOMER	LOCATION	APPLICATION	START-UP
Sodra Skogsagarna AB	Monsteras, Sweden	Oxygen Delig., C/D Bleach Swing Digester	1984
STFI	Stockholm, Sweden	Testing	1984
NCB AB	Vallvik, Sweden	Oxygen Delig., C/D E1 Bleach Digester Feedback	1984
MoDoCell AB	Husum, Sweden	Oxygen Delig., C/D E1 Bleach Digester Feedback	1985
AB Iggesunds Bruk	Iggesund, Sweden	C/D, E1 Bleach Digester Feedback, Carryover Comp.	1986
ASSI Frovifors Bruk AB	Frovi, Sweden	Fiber Identification Stock Prep. Refiner Control	1986
SCA Pulp AB	Ostrand, Sweden	Oxygen Delignification Digester Feedback	1986
Holmen Cell Kraft	Skarblacka, Sweden	(6) High Yield Batch Digester, Stock Prep., Refiner Control	1986
Holmen Cell Kraft	Skarblacka, Sweden	Oxygen Delignification Digester Feedback	1986
Norrsundet Bruk AB	Norrsundet, Sweden	Oxygen Delig., Kamyr C/D,. E1 Bleach	1987
STORA Cell	Skutskar, Sweden	(3) Kamyr Control Oxygen Delignification	1987
STORA Cell	Skutskar, Sweden	Oxygen Delignification C/D, E1 Bleaching	1987
MoDoCell AB	Husum, Sweden	(2) C/D, E1 Bleach (8) Batch Digester	1987
Soda Skogsagarna AB	Morrum, Sweden	Oxygen Delignification Batch Digester	1987
Korsnas AB	Gavle, Sweden	Oxygen Delignification Digester Feedback	1988
Champion International	Pensacola, FL	Oxygen Delignification Digester Feedback	1988
STORA Cell	Gruvon, Sweden	Oxygen Delignification Digester Feedback	1988
ModoCell AB	Domsjo, Sweden	Sulfite Digester C/D, E1 Control	1988
ASSI Kraftliner	Lovholmen, Sweden	High Yield Digester	1989
Willamette Industries	Bennettsville, SC	RDH Digester Oxygen Delig., C/D, E1	1989
Oji Paper	Japan	Oxygen Delignification	1989
Willamette Industries	Hawsville, KY	C/D, E1 Bleach (5) Batch (Hardwood)	1989
Jujo Seishi	Yatsushiro, Japan	Oxygen Delignification	1989
Kymmene AB	Jakobstad, Finland	Blowline sampling	1989
Bahia Sul	Brazil	Oxygen Delignification	1990
Akita	Japan		1990
Champion International	Pensacola, FL	Blowline sampling	1990
Nekoosa Papers, Inc.	Nekoosa, WI	Bleach Plant Control	1990

TABLE VI- (CON'T)

WORLDWIDE STFI OPTI-KAPPA® INSTALLATIONS REFERENCE LIST[a]

CUSTOMER	LOCATION	APPLICATION	START-UP
Willamette Industries	Hawsville, KY	#2 Bleach Line	1990

[a] Source: Asae Brown Boveri (ABB) Industrial Systems, Inc.

EMERGING TECHNOLOGIES

SLC® EXTRACTION PROCESS

Technology Description:

Suppressed lignin condensation (SLC) is a proprietary process designed to reduce the amount of dissolved lignin that precipitates back onto fibers following the C-stage of bleaching. This is accomplished by separating the liquid phase of the alkali treated chlorinated pulp after one to two minutes of reaction, treating that liquid and then returning the liquid to the pulp. This process results in a reduction of the CEK number thereby reducing the amount of chemicals needed in subsequent bleaching stages.[24]

Effectiveness:

Pilot plant studies have been performed at two facilities, one a softwood kraft and the other a hardwood kraft mill.[24] Results of these studies showed a reduction in CEK of 26 and 24% for softwood and hardwood, respectively.[24] Also shown was a reduction in chlorine consumption by ten% while maintaining the same reduced CEK number.[24] This reduction in CEK number resulted in a 47.2% reduction in the amount of hypochlorite needed in subsequent bleach stages for hardwood pulp.[24] No figures were provided for softwood pulp.

Installations:

No full scale application have been reported.

Implementation:

SLC is an add-on process, requiring minimal alteration of existing process units. Additional equipment needed for the SLC process include a low consistency mixer, holding tank, thickener, filtrate tank and a small filtrate reactor with heating provisions.[24] Process availability is uncertain, due to its proprietary nature.

Costs:

Capital and operating and maintenance costs are unknown. Chemical savings based on reduced bleaching requirements have been estimated at $4.41 per air-dry ton.[24] In addition, reduced steam usage has been predicted that would result in additional cost savings of $1.35 per air-dry ton.[24]

References:

24

RAPSON-REEVE CLOSED CYCLE

Technology Description:

The Rapson-Reeve process is based on eliminating discharges from the bleach plant by recycling the bleach plant filtrates to the pulp mill. The organics in these filtrates are incinerated in the recovery boiler, the sodium chloride introduced in the process from the use of chlorine based bleach chemicals is removed through the Salt Recovery Process (SRP) and the salt cake produced is used as make up chemical for chlorine dioxide production. The concept of this process and its details have been published in numerous articles, three of which are included in the reference list attached to this paper.[148,155,161]

Effectiveness:

The process was conceived to completely eliminate the discharge from the bleach plant. In actuality the facility ran in the range of 50-70% recycle of the filtrate streams due to problems encountered.[161]

Installations:

This technology was applied full scale at the Great Lakes Forest Products Limited (now Canadian Pacific Forest Products Limited) bleached kraft mill, ('B' mill) in Thunder Bay, Ontario, Canada. The mill was started up in November 1976 and the recovery of bleach plant effluent began in March 1977 with completion of the SRP. In 1988, mill management decided to abandon the process and build an external wastewater treatment system in order to meet the Province's waste discharge limitations. At the present time there are no installation of the Rapson-Reeve Closed Cycle technology in operation, although interest in the process remains high. With the great reductions in chlorine usage made through extended delignification, oxygen delignification, oxygen extraction and high chlorine dioxide substitution and the resolution of the problems encountered as discussed below,this process may prove to be technically and economically feasible.

Implementation:

As expected with any new process of this magnitude there were a number of operating problems encountered with start-up. Many of these were resolved through minor process modification, however even after these modifications were made, the facility was not able to achieve total recycle of the bleach plant filtrates. Some of the problems encountered are as follows:

(1) Corrosion - Even though considerable effort was spent in the selection of metallurgy for the closed-cycle system, corrosion problems were encountered. Within two years corrosion of the recovery furnace superheater caused tube failure and the tubes had to be replaced. As a result of this the system operated at a lower recycle rate to reduce the chloride buildup

(2) Pitch buildup - When the mill switched to alternating between softwood and hardwood pitch buildup became a problem when aspen was pulped and the quality of the product could not be maintained.

(3) Chemical recovery - The high chloride content of the liquor caused a reduction in the temperature of the smelt causing a problem with bed maintenance.

(4) Causticizing area - During closed cycle operation problems were encountered with lime reactivity and lime settling.

Costs:

The capital cost of the entire bleach plant is reported to have cost $8 million in 1977. The operation cost for this system based on 1979 data (assuming 0.80 US dollar/Canadian dollar) was estimated to be $5.99/air dried ton of pulp.[148] This cost includes the costs of steam production and consumption, bleach chemical consumption, salt production, defoamer use, treated water consumption, operating cost of salt recovery process plant and the increased cost of high ClO_2 substitution.[148] Not included in these costs were costs of installation or costs associated with the higher equipment replacement cost as compared to a conventional mill due to the reduced life of equipment caused by increased corrosion.[148]

References:

148, 155, 161

VII. WASTEWATER TREATMENT TECHNOLOGY

PHYSICAL/CHEMICAL TREATMENT

ULTRAFILTRATION

Technology Description:

As seen in **Table II-2** and discussed previously, approximately 75% of the chlorinated organics by weight in the spent extraction liquor have a molar mass greater than 10,000 g/mole. For the separation of molecules of this size, membrane technology can be used. The membrane process ultrafiltration utilizes a semipermeable membrane for separation purposes. These membranes can be specified by the size of the molecules they retain. Four different configurations are available: tubular, hollow fiber, flat sheet, and spiral wound. By using a pressure drop across the membrane, a permeate of water and low molar mass compounds go through the membrane, while a concentrate of the high molar mass compounds are retained on the feed side. The concentrate can be disposed of by incineration in the recovery furnace as is practiced by two Japanese mills employing the technology.[32]

Effectiveness:

A number of investigators have reported on the use of ultrafiltration for the treatment of pulp and paper mill waste streams. Test results from a Canadian kraft mill provided below in **Table VII-1** showed that 65% of the organically bound chlorine was separated into a concentrate stream that was 6% of the feed flow.[32] Based on actual mill-site tests, color removals of 86% were obtained.[32]

TABLE VII-1
ULTRAFILTRATION TRIAL RESULTS[32]

Effluent Feed		Filtrate, % of Feed	Concentrate, % of Feed
Flow:	10.3 m^3/adt	94	6
BOD:	13.5 kg/adt	55	45
COD:	63,0 kg/adt	34	66
Colour:	332.8 kg/adt	13	87
Total Solids:	116.3 kg/adt	67	33
Organics:	39.9 kg/adt	34	66
Cl^-:	31.7 kg/adt	97	3
Organic Chloride:	4.2 kg/adt	35	65
Na^+:	30.7 kg/adt	88	12
Resin & Fatty Acids:	104.6 g/adt	30	70
Total Chlorinated Phenols:	36.0 g/adt	100	0

Tests by Lundahl at the Iggesund, Sweden mill show similar results.[147] These data compare very well to actual performance data for three mills provided in **Table VII-2.** These studies also show that the ultrafiltration membranes do not reject chloride ions. Lundahl also showed that ultrafiltration caused no significant reduction in the toxicity of the E-stage effluent.[147]

TABLE VII-2

EFFLUENT REDUCTION DATA FOR COMMERCIAL ULTRAFILTRATION PLANTS[88,116,164]

	Sanyo Pulp Mill	Taio Paper Co.	MoDoCell
COD Reduction, (%)	82	79	65
Color Reduction, (%)	94	-	-
AOX Reduction, (%)	-	-	70
Chlorophenols Reduction, (%)	-	-	10-20

Installations:

Three installations are referenced in the literature. These include two in Japan, Sanyo Kokusaku Pulp Mill and Taio Paper Company, and one in Sweden, MoDoCell at Husum.[88,116] The Sanyo mill treats only the E-stage effluent from its hardwood line which constitutes about one third of its total production.[148] The Taio Paper Co facility is a large complex including facilities for producing bleached kraft pulp, semi-bleached pulp, unbleached kraft pulp, TMP, groundwood pulp and deinked waste paper. At this facility the E-stage effluent from the bleached kraft mill is treated.[148] The Husum mill also treats the E-stage effluent from its facility.

Implementation:

Technical problems associated with the ultrafiltration process as applied to bleach plant effluents have been identified by Jain and include the following:[148]

(1) Low initial flux rates and gradual decline in flux rates with time of operation.

(2) Effect of burning ultrafiltration concentrate on chloride buildup in the chemical system, and its impact on the recovery process, particularly at those facilities that do not have high SO_2 emissions, and , consequently, cannot purge chlorides as HCl from recovery furnaces.

(3) Absence of technologies for final disposal of the ultrafiltration concentrate if burning in the recovery furnace is not feasible.

(4) Inadequate information on the nature of membrane deposits, and procedures for cleaning membranes to restore their initial flux rates.

No information could be found as to the time required for design and construction of these facilities.

Costs:

Jonsson reports that the E-stage effluent from a kraft pulp mill can be treated by ultrafiltration for less than one% of the sales value of bleached kraft pulp.[88] The estimated total annual cost of 25 SEK per metric ton of pulp was reported by Jonsson.[88] This cost includes an amortized capital cost of 12 SEK per metric ton based on an interest rate of 15% and a pay back period of ten years and an operating cost of 24 SEK per metric ton, and credits of 11 SEK per metric ton.[88] The operating costs include electricity, cleaning, membrane replacement and evaporation of condensate and the credits include the heat value of the condensate and the recovery of sodium. In these cost estimates actual costs from the two Japanese facilities for electricity, cleaning and membrane replacement were utilized.[88] Dorica, et al, estimated the fixed capital investment (equipment cost x 2) for complete effluent recycling of bleach plant effluents using combinations of ultrafiltration and reverse osmosis at $20.5 million (CDN) and $42.5 million (CDN) for a 625 od ton/day and 890 od ton/day, respectively.[32] Of these costs, $1.17 million (CDN) and $3.51 million (CDN) were for the ultrafiltration of the extraction wastestream.[32]

References:

32, 35, 85, 88, 116, 117, 127, 147, 148, 164, 178

CHEMICALLY ASSISTED CLARIFICATION

Technology Description:

Dissolved and colloidal particles in wastewater streams are not readily removed from solution by simple settling. Chemically assisted clarification (CAC) consists of adding various chemicals to wastewaters for the purpose of precipitation, flocculation, coagulation or agglomeration in order to change the state of the pollutant or to cause it to be removed through physical means such as sedimentation or flotation. Chemicals in common use include lime, alum, ferric chloride, ferric sulfate, magnesia and a myriad of polyelectrolytes. A number of CAC processes have been patented including the lignin removal process (LRP) and the Hansel process.

The LRP process consists of adding acidified sludge to the waste stream to be treated, a retention period of 2-4 minutes, adjustment of the pH to 4.6-5.3 with lime or caustic, polymer addition (1-4 mg/l), and sedimentation for 2-4 hours.[84] The majority of the settled sludge (80-90%) is recirculated back to the beginning of the process.[84]

The Hansel process involves the use of certain polymers used in the past but at lower dosages due to a technical advance which has been patented. It is claimed that the additive concentration in the Hansel process are at least an order of magnitude lower, that the sludge created is denser and that the character of the sludge makes it easier to dewater than traditional alum-based sludges.[125]

For the most part use of CAC in the pulp and paper industry in the past has been for the purpose of reducing the color in the wastewater. The source of the color is large molecular organic compounds derived from the natural lignin and tannins in the wood.

Effectiveness:

Bench scale studies were performed by EPA to determine if CAC was a viable treatment technology for the removal of 2378-TCDD and 2378-TCDF. These investigations demonstrated that more than 95% of the 2378-TCDD and 2378-TCDF in the caustic extraction stage and in the combined bleach plant wastewaters were removed through use of CAC.[2] These removals were achieved at substantial dosages of alum (2000 mg/l) or lime (1500 mg/l) plus the addition of polyelectrolytes.[2] In addition, studies performed on the aeration basin mixed liquor showed that a limited improvement in the removal efficiency for 2378-TCDD and 2378-TCDF were achieved through the use of polymers.[2] Studies on the final effluent showed marginal improvement in effluent quality for TSS and 2378-TCDF.[2] Results of these studies are provided in **Table VII-3.**

NCASI also performed a screening study of the treatability of dioxins and furans in bleach plant filtrates and mill wastewaters. Results of these investigations were similar to those reported by EPA. Removals in excess of 98% were observed in bleach plant filtrates at coagulant dosages of 9000 mg/l lime or 9000 mg/l alum.[27] Studies performed on the final effluent resulted in nondetectable levels of 2378-TCDD and 2378-TCDF with removal rates in

TABLE VII-3

USEPA BENCH SCALE WASTEWATER TREATABILITY STUDY RESULTS - MILL A[2]

	UNTREATED	TREATED	% REMOVAL	TREATMENT
Caustic Extraction				
TSS	40	18	55	Alum (2000 mg/l)
TOC	290	150	48	Nalco 7769 (7.5 mg/l)
2378-TCDD	0.50	<0.019	>96	(anionic)
2378-TCDF	2.15	<0.039	>98	
Combined Bleach Plant				
TSS	86	19	78	Lime (1500 mg/l)
TOC	190	120	37	Calgon WT 2439
2378-TCDD	0.20	<0.010	>95	(5.0 mg/l)
2378-TCDF	0.88	<0.011	>98	(cationic)
Aeration Basin Effluent				
TSS	3700	70	98	Gravity Settling
TOC	400	57	86	No Additives
2378-TCDD	0.84-0.85	<0.030	>96	
2378-TCDF	2.63	0.091	>96	
Aeration Basin Effluent				
TSS	3700	17	>99	American Cyanamid
TOC	400	48	88	1906 N (6.25 mg/l)
2378-TCDD	0.84-0.85	<0.016	>98	(non-ionic)
2378-TCDF	2.63	<0.016	>99	
Final Effluent				
TSS	23	15	35	Alum (200 mg/l)
TOC,	48	22	54	Calgon 2136 (4.0 mg/l)
2378-TCDD	0.009-0.012	<0.043	-	(cationic)
2378-TCDF	0.043	<0.02	>53	

NOTE: 1. Use of products or mention of trade names does not constitute endorsement.
2. Analyses for TSS and TOC by E.C. Jordan Co.
3. Analytical results for total suspended solids (TSS) and total organic carbon (TOC) are reported in mg/l (or ppm); analytical results for 2378-TCDD and 2378-TCDF are reported in pg/gm (or ppt).

excess of 88% at coagulant dosages of 2500 mg/l lime or 2500 mg/l alum.[27] Results of these investigations are provided in **Table VII-4.**

Studies were also performed by NCASI on the same wastewaters using only polymer. These studies showed that 93-94% removal of 2378-TCDD and 2378-TCDF could be achieved in the secondary treatment influent at dosages of 2-20 mg/l and that at polymer dosages ranging from 4-12 mg/l 2378-TCDD removals of 18-27% and 2378-TCDF removals of 35-54% could be achieved in the secondary effluent.[27]

TABLE VII-4

NCASI RESULTS OF 2378-TCDD AND 2378-TCDF ANALYSES FOR TREATMENT OF KRAFT MILL "A" EFFLUENTS[27]

	UNTREATED	TREATED	% REMOVAL	TREATMENT
Bleach Plant Filtrate				
2378-TCDD	1.5	1.2	20	Lime (500 mg/l)
2378-TCDF	37	37	0	
Bleach Plant Filtrate				
2378-TCDD	1.5	ND(0.027)	>98	Lime (9000 mg/l)
2378-TCDF	37	0.23	99	
Bleach Plant Filtrate				
2378-TCDD	1.5	1.2	20	Alum (500 mg/l)
2378-TCDF	37	31	16	
Bleach Plant Filtrate				
2378-TCDD	1.5	0.021	99	Alum (9000 mg/l)
2378-TCDF	37	0.23	99	
Final Effluent				
2378-TCDD	0.093	0.050	46	Lime (200 mg/l)
2378-TCDF	2.6	1.4	46	
Final Effluent				
2378-TCDD	0.093	ND(0.011)	>88	Lime (2500 mg/l)
2378-TCDF	2.6	ND(0.006)	>99	
Final Effluent				
2378-TCDD	0.093	0.048	48	Alum (200 mg/l)
2378-TCDF	2.6	0.98	62	
Final Effluent				
2378-TCDD	0.093	ND(0.006)	>94	Alum (2500 mg/l)
2378-TCDF	2.6	ND(0.008)	>99	

Pilot plant studies performed utilizing the LRP process showed that up to 70% removal of TOCl, 95% of color and 59% of chlorinated phenol could be achieved treating the total mill waste for a softwood kraft mill.[84] Similar studies on hardwood kraft resulted in lower removal rates. Results of these studies are presented in **Table VII-5.**

Studies done at the Champion Canton mill utilizing the Hansel process are reported to have resulted in the reduction of color from an influent ranging from 1,000-1,200 Pt-Co color units (PCU) to 80 PCU, resulting in the production of 1.36 pounds of sludge per 1000 gallons of waste treated at a solids content of 2.5-3%.[125] Data related to the ability of the Hansel process to remove dioxin consists of two tests, one where a river water sample at 16 ppq was reduced to ND(5 ppq) and another were a effluent sample spiked to 326 ppq was reduced by 89%.[125]

Laboratory studies performed on total bleach plant waste where alum was used resulted in a COD reduction of 40-60%, a BOD_7 reduction of 25% and a reduction in TOCl of 60-70%.[1]

TABLE VII-5

LRP EFFLUENT TREATMENT RESULTS[84]

	TOTAL MILL EFFLUENT PERCENT REMOVAL	
	KRAFT SOFTWOOD	KRAFT HARDWOOD
BOD_7	0-20	0-20
COD	22-67	20-41
Color	32-95	21-33
TOCl	36-70	30-31
Chlorinated Phenols	50-59	32-44

Installations:

There are no known full scale applications of CAC on bleached pulp mill waste. CAC is, however, being used at the Stone Container mill at Hodge, LA. In this application polyelectrolyte is being added to the effluent for color removal.

Implementation:

Implementation of the LRP process consists of retrofitting an existing primary clarifier and involves installation of chemical storage, piping, tanks, electrical controls and foundations for buildings.[84] The two most commonly encountered problems with this technology are the amount of solids produced and the difficulties associated with dewatering and disposal. No information was available as to the time needed for installation of a CAC system.

Costs:

Costs for CAC are highly dependent on the amount of coagulants used and the amount of solids produced. The cost of reagents for the Hansel process are reported as ranging between 12¢ and 22¢/1000 gallons of 1,200 PCU.[125] The costs for a 20 MGD facility are reported as follows: capital cost of $1.85 million, operating costs of $15/1000 gal, $3,000/day or approximately $1.095 million/year and a price per ton of production of approximately $3.40.[125]. These costs, however do not include sludge disposal. The costs for retrofitting a primary clarifier for the LRP process based on a 400 Ton/day CTMP facility were reported as a capital cost of $370,000 and operation costs of $520,000/year.[84] The operation costs include chemicals, power, sludge handling, analysis and control, and maintenance.[84]

References:

1, 2, 27, 84, 125, 128

ENHANCED PHOTOOXIDATION

Technology Description:

This process involves the use of ultraviolet light and hydrogen peroxide to oxidize hazardous and biorefractory organic wastes. This is accomplished through the production of hydroxyl free radicals from ultraviolet light induced decomposition of the hydrogen peroxide. The hydroxyl free radicals produced are highly reactive but are reported to be non selective in that they oxidize recalcitrant molecules as easily as those that are biodegradable.[203]

Effectiveness:

Two trials of this process are reported in the literature, one on pine Eo filtrate at a South Carolina mill and the other on a Canadian bleach plant effluent.[203,205] AOX reductions were reported by one source to be from approximately 3.5-4.0 kg/tonne to 2.5 and 1.,5 kg/tonne.[205] Color removal was reported by one source to be greater than 98 percent (5000 PCU to <100 PCU) while a second source reported a color removal rate of 80 percent.[203,205] One distinct advantage of this process over other color treatment processes is that no sludge is generated.[205]

Installations:

There are no installations of this technology referenced in the literature reviewed.

Implementation:

The time required to implement this process was not provided in the literature reviewed.

Costs:

The capital cost associated with this process was estimated by one source to be approximately $8-9 million for an 800 tonne per day mill with an influent AOX of 4.5 kg/tonne and a treated effluent AOX of 2.5 kg/tonne.[205] The operating cost was given as approximately $4.50/tonne of pulp produced.[205] Another source stated that this treatment process had an operating cost that was competitive with other color removal technologies.[205]

References:

203, 205

BIOLOGICAL TREATMENT

AEROBIC TREATMENT

Technology Description:

Biological treatment is utilized for the treatment of pulp and paper wastewater due to the relative biodegradability of most of the organic substances in the waste, with the exception of lignin. The most common biological treatment used in the industry is aerobic treatment either in the form of aerated stabilization basins (ASB) or activated sludge. ASBs or aerated lagoons are used all over the world and are common in Sweden and the US. In these systems aeration is accomplished through mechanical surface aeration or through the use of diffused air. Retention times are normally in the range of eight to ten days but are frequently up to 15 days. The main advantages of ASBs are lower energy requirements, lower operational attention required, lower capital cost where land costs are low, and good equalization of hydraulic and organic loads. Activated sludge systems are similar to the ASB except that they treat the wastewater in a shorter period of time, usually being designed for four to eight hours of total retention. Activated sludge systems are preferred to aerated lagoons in many countries due to the fact that they are more compact and give a somewhat better and more uniform reduction on BOD and COD.[35]

Effectiveness:

Aerated biological treatment, especially activated sludge, has been shown to be effective in the removal of chlorinated organic matter achieving AOX removals of 48-65% and chlorophenolics removals of 75-95%.[77] Aerated stabilization basin systems were also effective, but to a lesser degree achieving 32% removal of AOX and 54% removal of chlorophenolics.[77] The main reason(s) for this difference in efficiency is reported to be related to solids retention time or to the fact that in aerated lagoon systems materials that are adsorbed onto the cells are liberated back into the liquid phase when the cells decompose, while in the activated sludge systems the excess solids are removed from the system.[35] In another study conducted at a mill utilizing oxygen delignification the AOX reduction across the ASB after seven days of detention was 56% achieving a final AOX level in the treated effluent of 1.28 kg/ADT.[160] As a summary of removal efficiencies, **Table VII-6** presents design criteria for four aerobic systems, two ASBs and two activated sludge.

Little data exist to show what the removal efficiency of aerobic treatment systems is for 2378-TCDD and 2378-TCDF. A preliminary comparison was made however of 2378-TCDD discharged from kraft mills with activated sludge treatment and aerated stabilizations basins. On a mean basis. the concentration, mass, and mass per unit of production of 2378-TCDD discharges are somewhat higher from mills with ASB treatment as shown in **Figure VII-1.**

Installations:

At the present time 101 of 104 of the chemical pulp mills that bleach with chlorine utilize aerobic biological treatment systems for the treatment for their wastewaters. Of these, approximately 50 percent utilize ASBs and 50

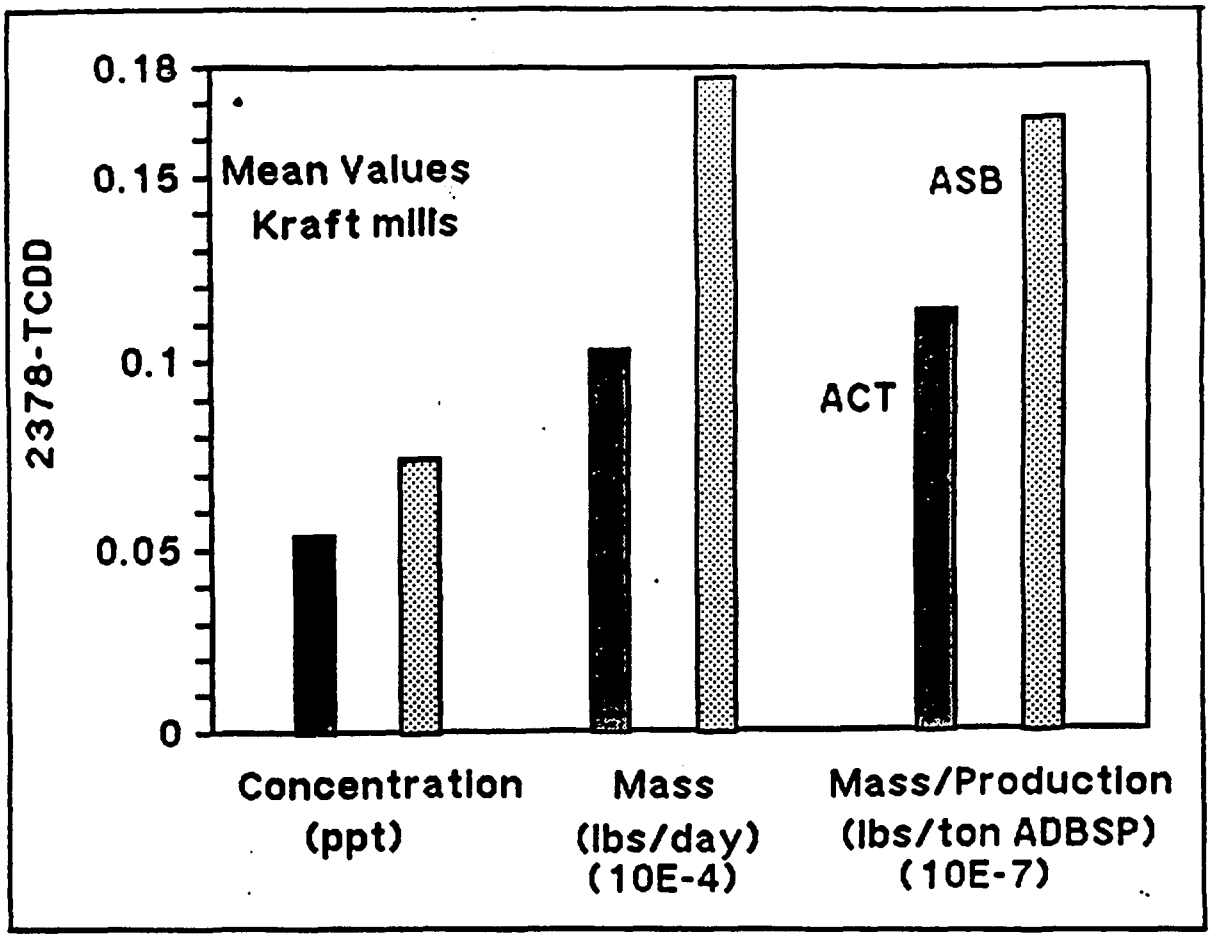

FIGURE VII-1 2378-TCDD IN ACTIVATED SLUDGE AND AERATED STABILIZATION BASIN WASTEWATER EFFLUENTS

percent utilize activated sludge systems.[163] In Sweden seven of 15 bleached kraft mills, constituting approximately 40% of permitted production, have secondary biological wastewater treatment, see Table V-5.[116]

TABLE VII-6

TYPICAL PARAMETERS FOR PULP AND PAPER BIOLOGICAL WASTEWATER TREATMENT PLANTS[85]

	AERATED STABILIZATION BASIN	AERATED STABILIZATION BASIN	ACTIVATED SLUDGE	ACTIVATED SLUDGE
Retention Time, hours	120	240	10	24
F/M ratio	0.8	0.5	0.3	0.12
Chloroform Reduction, %	90	95	90	95
Chlorinated Phenolics Reduction, %	25	50	60	80
AOX Reduction, %	10	30	40	60

Implementation:

The time required for installation of this technology is somewhat dependent on the choice of system employed with activated sludge systems usually requiring more time than aerated stabilization basins. An appropriate time for implementation of this technology would be two years. This figure is based on experience gained during the late seventies when the majority of biological wastewater treatment systems in the industry were installed.

Costs:

Costs related to this technology were not found in the literature reviewed for this report but are readily available. Recommended sources include the following: Treatability Manual Volume IV Cost Estimating, Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C., EPA-600/2-82-001d, April 1983 (Revised) and Development Document For Effluent Limitations Guidelines (BPCTCA) for the Bleached Kraft, Groundwood, Sulfite, Soda, Deink and Non-intregrated Paper Mills Segment of the Pulp, Paper, and Paperboard Point Source Category, U.S. Environmental Protection Agency, Washington, D.C., EPA 440/1-76/047-b, December 1976.

References:

7, 27, 35, 37, 73, 76, 77, 84, 93, 101, 102, 121, 127, 160, 175, 178, 180, 184, 193

ANAEROBIC TREATMENT

Technology Description:

Biological treatment of organic wastes can take place in anaerobic (oxygen-free) conditions. Such conditions can take place in deposited sludge at the bottom of aerated lagoons. Anaerobic systems are based on the production of anaerobic bacteria, anaerobes, which grow slower and require less energy and nutrients than aerobic bacteria. End products of anaerobic decomposition includes methane gas and water. Advantages of anaerobic over aerobic treatment are that less sludge is produced, little energy is required to run the system and energy in the form of the methane gas is produced.

Effectiveness:

Anaerobic degradation and dehalogenation of low molecular chlorinated organics has been known for some time and is reported in the literature.[35] One study of anaerobic treatment of bleach plant waste reported 70-90% removal of chlorophenols, 70-90% removal of chloroform and 20-30% removal of TOCl at a hydraulic loading of $3.5m^3/m^3$ of reactor/day.[35] This degree of TOCl removal, which was achieved in seven hours, was reported as the same as that achieved in an aerobic treatment system in seven days.[35] In another study, permeate from ultrafiltration of E1-stage filtrate was added to the C/D filtrate and treated anaerobically. AOX was reduced from 92 mg/l to 67 mg/l (27% removal) with a retention time of one hour and from 92 mg/l to 42 mg/l (54% removal) with a retention time of 24 hours.[35]

Installations:

Several anaerobic wastewater treatment systems are in operation in the pulp and paper industry with the majority at sulfate and CTMP facilities. Two ENSO-FENOX system are reported in operation in Finland treating bleach plant effluents.[35]

Implementation:

Anaerobic systems need aerobic systems to polish the wastes prior to discharge. Anaerobic systems tend to work best on concentrated wastes as high biological solids levels are needed to obtain good organic removals. If a dilute waste is treated, the problem becomes keeping the solids in the reactor from being washed out of the system. The reason why anaerobic systems have not been utilized more in the kraft pulping industry stems from the fact that the few waste streams that are organically concentrated enough to treat anaerobically tend to exhibit toxicity toward the anaerobic organisms.

Costs:

No information was available in the literature reviewed related to costs for anaerobic systems.

References:

7, 21, 35, 85, 116, 142, 163

ATTACHMENT A
REFERENCES

ATTACHMENT A - REFERENCES
TECHNOLOGIES FOR THE CONTROL AND REDUCTION OF CHLORINATED ORGANICS FOR THE PULP INDUSTRY

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
1.	Treatment Of Effluents From The Pulp And Paper Industry By Chemical Coagulation	Almemark, M.; Eriksson, G.; Hagerstedt, L.-E.	TAPPI Seminar Proceedings, Bleaching and the Environment, Seattle, Washington, September 1988, pp. 251-272.	This paper deals with chemical coagulation of bleach plant effluents with alum followed by incineration of the sludge and acid recovery of the coagulants. Costs are projected for full scale operation.
2.	Bench Scale Study of Dioxins and Furan (2378-TCDD and 2378-TCDF) Treatability in Pulp and Paper Mill Wastewaters	Amendola, G.A.; Bodien, D.G.; Handy, R.E.Jr.	TAPPI Journal, December 1989, pp. 189-194.	The principal objectives of this study were to determine the solid and liquid phase distribution of 2378-TCDD and 2378-TCDF in untreated, partially treated and treated process wastewaters from pulp and paper mills; and to determine whether chemically assisted clarification (CAC) might be a feasible alternative for removing those compounds from internal mill and total mill process wastewater. Results of bench scale studies indicate that from 30% to 40% of the 2378-TCDD and 2378-TCDF is present in the solid phases of internal mill samples; greater than 90% in aeration basin effluents; and from 40% to 75% in final effluents. CAC proved to be effective at removing 2378-TCDD and 2378-TCDF from internal mill wastewaters, however, less cost effective than providing improved treatment in existing secondary treatment facilities.
3.	On-Line Oxygen Delignification Control	Anon.	TAPPI/CPPA Proceedings, 1988 International Pulp Bleaching Conference, Orlando, Florida, June 1988.	Discussion of control system for oxygen delignification based on on-line Kappa number measurement. System reduced average Kappa number and production costs.
4.	P & P's Annual Bleaching Survey: Capital Expenditures Increasing	Ducey, M.J., Technical Editor	Pulp & Paper, June 1988, pp. 72-75.	General summary of capital expenditures in bleached pulp mills. chlorine dioxide substitution, oxygen delignification, and process control are a big part of capital expenditures.
5.	Oxygen Bleaching of Kraft Pulp: High Consistency vs. Medium Consistency	Idner, K.	TAPPI Journal, February 1988, pp. 47-50.	A comparison between conventional high-consistency bleaching and medium-consistency oxygen bleaching is reported. Associated pulp viscosity and Kappa number, costs, and environmental effects are provided.
6.	Extended Delignification, An Alternative To Conventional Kraft Pulping	Mera, F.E.; Chamberlin, J.L.	TAPPI Journal, January 1987, pp. 132-136.	Mill and pilot plant data for market grade bleached pulp were evaluated. The pulp quality was equivalent to or better than that of bleached pulps obtained by conventional kraft pulping and bleaching techniques. However, operating parameters favored extended cooking in the rapid displacement heating process. These parameters were lower active alkali consumption, lower bleaching chemical demand, and lower bleach plant effluent liability.

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TECHNOLOGIES FOR THE CONTROL AND REDUCTION OF CHLORINATED ORGANICS FOR THE PULP INDUSTRY

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
7.	Biosorption Of Organic Halide In Kraft Mill Generated Lagoon	Amy, G.L.; Bryant. C.W.; Alleman, B.C.; Barkley, W.A.	Journal WPCF, August 1988, pp. 1445-1453.	Kraft mill wastewater contains substantial concentrations of both total organic halide (TOX) and low molecular weight (less than 1000 g) TOX as a consequence of chlorine bleaching activities. An aerated lagoon removes from one-third to on-half of both these fractions of organic halide. Indirect evidence suggests that anaerobic degradation and dehalogenation occur in the benthal layer of the lagoon. Sorption onto settling biomass is the mechanism required for transport to the benthal layer. Aerobic biomass is capable of adsorbing both high and low molecular weight TOX; adsorption is affected by pH, temperature, cell age, and cell viability.
8.	Oxygen Bleaching Practices And Benefits - An Overview	Tench, L.; Harper, S.	TAPPI Proceedings, 1987 International Oxygen Delignification Conference.	A list of the world-wide oxygen delignification installations and a summary of the experience gained to date are presented. Pulp quality, environmental benefits, chemical savings, the impact on recovery and energy consumption, high vs. medium consistency delignification and washing and screening considerations are discussed.
9.	Reactions of Nitrated Kraft Lignin in an Alkaline Oxygen Bleaching State	Lindeberg, O.; Walding, J.	TAPPI Journal, October 1987, pp. 119-123.	Discussion on pretreatment of kraft pulp with NO2/O2 prior to oxygen bleaching and resulting chemical and selectivity effects.
10.	PRENOX® Process-Experiences from a Pilot Plant Installation, The	Simonson, O.; Lindstrom. L.-A.; Marklund, A.	TAPPI Journal, August 1987, pp. 73-76.	Study showing that high-consistency treatment of pulp with NO2 and O2 before the oxygen delignification stage can produce pulp with a kappa number of 7 and significantly reduce bleach-plant pollutants.
11.	Oxygen Bleaching's Pace Quickens	McDonough, T.J.	TAPPI Journal, August 1987, pp. 125-127.	General overview of discussions that occurred at the first International Oxygen Delignification Conference, June 7-12, 1987, San Diego, California.
12.	RDH Kraft Pulping to Extend Delignification, Decrease Effluent, and Improve Productivity and Pulp Properties	Andrews, E.K.	TAPPI Journal, November 1989, pp. 55-61.	Rapid displacement heating kraft pulping impacts on pulp bleachability and bleach plant effluent described in combination with brownstock oxygen delignification.
13.	Underchlorination Can Become Inadequate Medicine	Annergren, G.E.; Lindblad, P.-O.; Norden, S.	Svensk Papperstidning, November 12, 1987, pp. 29-32.	Underchlorination was in earlier times something negative and regarded clearly as harmful for pulp. The technical development has however waited to be understood--today underchlorination is something to strive for, not the least from the environmental standpoint. This paper discusses the studies of reduced chlorine usage on pulp properties.
14.	North America's First Fully Integrated, Medium Consistency Oxygen Delignification Stage	Enz, S.M.; Emmerling, F.A.	TAPPI Journal, June 1987, pp. 105-112.	Consolidated Papers Inc. has installed a medium-consistency oxygen delignification reactor in the hardwood pulp line at its kraft mill in Wisconsin Rapids, Wisconsin. System has resulted in a decrease in kappa number, increased production and brightness and a decrease in chemical consumption.

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TECHNOLOGIES FOR THE CONTROL AND REDUCTION OF CHLORINATED ORGANICS FOR THE PULP INDUSTRY

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
15.	Effect Of Prebleaching Conditions On The Performance Of Short Sequences For Oxygen Bleached Kraft Pulp	Annergren, G.E.; Lindstrom, L.-A.; Lindblad, P.-O.; Norden, S.	TAPPI/CPPA Proceedings, 1988 International Pulp Bleaching Conference, Orlando, Florida, June 1988, pp. 37-46.	Important prebleaching conditions have been studied for short sequence bleaching both in the laboratory and in mills, The studies concerned mainly oxygen bleached kraft pulp but certain comparisons have been made with unbleached kraft pulp. There were two reasons for dealing with prebleaching in this case. A short sequence gives higher weighting to each stage which calls for a particular optimization of the prebleaching. On the other hand, environmental concerns aim at a low formation of chlorinated organics through a reduced chlorination. The general opinion is that a high chemical charge is required in the chlorination of a short sequence, However, our results indicate that this is not true for normal levels of final brightness and that commercial operation with a substantial restricted chlorination is possible, The reinforcement of the alkaline extraction is very important in this context.
16.	Pulping Bleaching Concerns Focus on ClO2 Generation, Effluent	Ducey, M.J., Technical Editor	Pulp & Paper, June 1987, pp. 89-92.	Article takes a comprehensive look at the current mill chemical consumption patterns, new supplier products and their markets and the latest developments from a number of North American research institutions, and provides some brief facts on worldwide chemical pulp production and growth over the past 12 months.
17.	Minimizing the Formation of Chlorinated Organic Material Through Controlled Chlorination in the Production of High Quality Softwood Kraft Pulp	Annergren, G.E.; Rees-Andersson, A.-M.; Lindblad, P.O.; McKague, B.; Stromberg, L.M.; Kringstad, K.P.	TAPPI Proceedings, 1987 Environmental Conference, Portland, Oregon, April 1987, pp. 313-318.	Spent liquors from the chlorination and alkali extraction of an oxygen prebleached softwood kraft pulp were investigated with respect to environmental parameters such as TOCl, chlorinated phenolic compounds some of which are lipophilic, other lipophilic compounds and mutagenicity. The results show that the parameters vary considerably with variations in the chlorine ratio and that therefore possibilities exist to minimize chlorinated organic compounds through controlling the chlorination.
18.	Laboratory Studies of Chloroform Formation in Pulp Bleaching	Crawford, R.J.; Stryker, M.N.; Jett, S.W.; Carpenter, W.L.; Fisher, R.P.; Jain, A.K.	TAPPI Proceedings, 1987 Pulping Conference, pp. 113-118.	The effects of C, E, and H stage bleaching parameters on chloroform production have been investigated in the laboratory for both softwood and hardwood kraft pulps. D stage chloroform production has been shown to be minimal. The H stage was found to be the largest chloroform producer.
19.	Improvement Of Bleach Plant Effluent By Cutting Back On Cl2	Axegard, P.	TAPPI/CPPA Proceedings, 1988 International Pulp Bleaching Conference, Orlando, Florida, June 1988, p. 69.	The consumption of Cl2 has been studied over a large range in a mill trial and in the laboratory. The results were evaluated for AOX, TOCl, EOCl, chloroform and chlorinated phenolics in the filtrate and as chlorodioxins and furans in the pulp. AOX and TOCl are reduced linearly with a decreased consumption of the elemental chlorine in Cl2 and ClO2. The ratio between AOX and TOCl is not constant which makes it difficult to translate a TOCl-value to an AOX-value. Chlorinated phenolics were found to be affected only by the Cl2-consumption. Below about 10 kg Cl2 ptp virtually no highly chlorinated phenolics could be found.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
20.	Effect of Chlorine Dioxide Substitution on Bleaching Efficiency and the Formation of Organically Bound Chlorine - Part II	Axegard, P.	Journal of Pulp and Paper Science, 1986.	
21.	Technical and Economic Aspects of Measures to Reduce Water Pollution caused by the Discharges from the Pulp and Paper Industry, The	COWIconsult	EEC-Contract B6612-551-88 Final Report, November 1989.	The report is a study of the technical and economical aspects of measures to reduce water pollution caused by the discharges of the pulp and paper industry. It is intended to be a development document for a future EEC Directive regulating aqueous discharges from this industry.
22.	Chlorine Dioxide Substitution Reduces the Load of TOCl	Axegard, P.	TAPPI Proceedings, 1987 Pulping Conference, November 1987, pp. 105-110.	Laboratory bleaching experiments have been carried out on an industrial oxygen delignified softwood kraft pulp at different ClO2 - substitution levels. Parameters studied were prebleaching efficiency, final brightness, formation of chlorate as well as chlorinated organics. The formation of TOCl, EOCl, AOX, highly chlorinated phenolics and chloroforms is reduced with reduced Cl2 consumption.
23.	Influence Of Bleaching Chemicals And Lignin Content On The Formation Of Polychlorinated Dioxins And Dibenzofurans, The	Axegard, P.; Renberg, L.	Chemosphere, (Dioxin 88)	The determination of chlorinated dibenzo-p-dioxins and dibenzofurans in pulp and aqueous filtrate from pulp bleaching showed that the most important variable is the consumption of molecular chlorine (Cl2) expressed as the ratio between chlorine and the lignin content (Cl2-multiple). The formation of the dioxins and dibenzofurans increased drastically above a certain critical level and below this level the formations were very low. No significant difference between oxygen delignified and non-oxygen delignified softwood kraft pulp could be established.
24.	Results of On-Site Pilot Plant Studies of the SLC® Extraction Process	Elton, E.F.; Parkinson, J.R.	TAPPI Proceedings, 1987 Pulping Conference, pp. 673-678.	The SLC® (suppressed lignin condensation) extraction process was pilot tested on hardwood and softwood kraft pulp in two separate mills. Reported results were decreased CEK No and decreased steam, hypochlorite (47%), and chlorine (10%) usage.
25.	Use of Hypolite Bleach in Short Sequence Pulp Bleaching, The	Hurst, M.M.; Sturik, T.S.; Duff, A.	TAPPI Proceedings, 1987 Pulping Conference, pp. 15-19.	Paper discusses brightness, viscosity and chloroform formation when replacing peroxide or hypochlorite with hypolite bleach, during pulp bleaching.
26.	Substituting Chlorine Dioxide For Elemental Chlorine Makes The Bleach Plant Effluent Less Toxic	Axegard, P.	TAPPI Journal, October 1986, pp. 54-59.	A full-scale mill trial shows there are two principal ways of reducing the consumption of elemental chlorine by using more chlorine dioxide when bleaching to full brightness. The methods used were "high substitution" and "low multiple." The formation of TOCl, EOCl and chlorinated acetic acids were found to decrease linearly with chlorine consumption.
27.	Screening Study of the Treatability of Dioxins and Furans in Bleach Plant Filtrates and Mill Wastewaters	Barton, D.A.; McKeown, J.J.; Brunck, R.A.	NCASI 1989 West Coast Regional Meeting, October 4, 1989.	Unpublished report consists of tables used for presentation at NCASI 1989 West Coast Regional Meeting.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
28.	Reinforcement of Oxygen-Alkali Extraction with Hydrogen Peroxide or Hypochlorite	Lachenal, D.; de Choudens, C.; Bourson, L.	TAPPI Journal, July 1986, pp. 90-93.	Small amounts of hydrogen peroxide or hypochlorite were added in the oxygen extraction stage of various bleaching sequences. The effects on viscosity and brightness are presented.
29.	Efforts in Chemical Pulp Bleaching Technology Emphasize Cutting Costs	Ducey, M.J., Technical Editor	Pulp & Paper, July 1986, pp. 47-50.	Article presents a summary of Pulp & Paper's third annual survey of bleaching equipment. Finds fewer new systems; emphasis is on washing, process control, chemical additions. Oxygen delignification is the number one choice of mills installing new systems.
30.	Curtailing Dioxin Formation-Ramifications for Chemical Pulp Bleaching	Berry, R.M.; et al.	Dioxin '89, September 1989	
31.	Oxygen Bleaching Processes	McDonough, T.J.	TAPPI Journal, June 1986, pp. 46-52.	Paper discusses many aspects of oxygen delignification, high and medium consistency, selectivity and protectors, pretreatment with nitrogen oxides, and process fundamentals. Also discusses oxygen extraction and low-pressure oxygen bleaching.
32.	Complete Effluent Recycling in the Bleach Plant with Ultrafiltration and Reverse Osmosis	Dorica, J.; Wong, A.; Garner, B.C.	TAPPI Proceedings, 1985 Pulping Conference, p. 590.	A membrane filtration process was studied for the treatment of bleach plant effluents using ultrafiltration and reverse osmosis. The objective was removal of color, organic compounds, and chloride ions. The filtration process design and costs are presented.
33.	Toward Preventing The Formation Of Dioxins During Chemical Pulp Bleaching	Berry, R.M.; Fleming, B.I.; Voss, R.H. Luthe, C.E.; Wrist, P.E.	Pulp & Paper Canada, 90(8), 1989, pp. 48-58.	Suitable combinations of chlorine multiple and CLO2 substitution which lead to low or undetectable levels of TCDD and TCDF have been identified. Adding chlorine to pulp in advance of chlorine dioxide has been found to be more effective than the reverse mode of addition for reduction of chlorinated dioxins and furans. Increasing the C-stage pH and decreasing its consistency also appears to be beneficial. Minimizing the levels of the precursors, dibenzodioxin (DBD) and dibenzofuran (DBF), was confirmed as being important for curtailing TCDD and TCDF formation. In particular, oxygen delignification was found to be advantageous, not because it removes lignin but because it decreases the precursor levels.
34.	Ozone Delignification of Black Spruce and Hardwood Kraft, Kraft-Anthraquinone, and Soda-Anthraquinone Pulps	Liebergott, N.; van Lierop, B.	TAPPI Journal, June 1981, pp. 95-99.	After ozone delignification followed by DED treatment, black spruce, and mixed hardwood kraft, kraft-AQ and soda-AQ pulps attained 89-92% brightness (ISO) and compared to conventionally bleached CEDED pulps, required less ClO2 in the third and fifth stages, had somewhat lower strength properties for black spruce but similar strength for hardwood pulps, and gave effluents and color loadings that were 60-75% lower.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
35.	Some Aspects On Biological Treatment Of Bleached Pulp Effluents	Boman, B.; Frostell, B.; Ek, M.; Eriksson, K.-E.	Nordic Pulp and Paper Research Journal, 1-1988 , pp. 13-18.	The article describes the most important methods presently used for external treatment of bleach plant effluents. They are in most cases designed to reduce BOD and are not very effective in reducing AOX. None of the biological methods currently used can degrade high molecular mass material. The possibility of using special fungi, able to attack the high molecular mass chlorinated lignins, is discussed. Anaerobic dechlorination is also mentioned. A combination of physical/chemical methods and biological treatment is proposed for the development of new purification processes. A combined process with ultrafiltration and effective biological treatment is estimated to give at least 95% reduction of BOD and 70-90% reduction of COD and AOX.
36.	Oxidation Of Pulp With NO2/O2 Prior To Oxygen Delignification - A Novel Process With Potentially Less Pollution	Brannland, R.; Lindstrom, L.-A.; Norden, S.; Simonson, O.	TAPPI Proceedings, 1985 International Bleaching Conference.	Four companies AGA, KemaNord, MoDo and Sunds Defibrator are jointly exploring a new delignification process. With this process, characterized by a pretreatment of pulp prior to oxygen delignification with a combination of NO2 and O2 it is possible to delignify softwood kraft pulp to kappa numbers below 10. In this paper we will discuss what impact this process will have on chemical composition and environmental effects of spent liquors produced in a subsequent bleaching process. Results will be compared with those from bleaching of oxygen delignified pulp. Also matters related to working environment and emission to air will be covered.
37.	Organic Halide In Kraft Mill Wastewaters: Factors Affecting In-mill Formation And Removal By Biological Treatment	Bryant, C.W.; Amy, G.L.	TAPPI Proceedings, 1988 Environmental Conference, pp. 435-438.	Chlorine is used as a pulp bleaching agent, resulting in the formation of various organochlorine compounds that range from simple chlorophenols to higher molecular weight chlorolignin compounds, In addition to persisting in the environment, some of these compounds exhibit toxicity or mutagenicity. Recent work has focused on the use of the total organic halide (TOX) parameter for measuring the totality of these compounds.
38.	Oxidative Bleaching - A Review, Part I: Delignification	Liebergott, N.; van Lierop, B.	Pulp & Paper Canada, September 1986, pp. 58-62.	Literature relating to the use of oxidative chemicals in the delignification and brightening operations of pulp bleaching is reviewed. Experimental data on the use of oxygen, ozone and chlorine dioxide in the chlorination stage and hypochlorite, peroxide and oxygen in the extraction stages are also presented.
39.	Factors That Affect The Generation Of Chloroform In Bleaching	Crawford, R.J.; Stryker, M.N.	TAPPI Journal, November 1988, pp. 151-159.	Bleachery filtrate mixing and pH adjustment in the mill effluent treatment system affect the formation of chloroform. In laboratory experiments, the pH adjustment of chlorination-stage filtrate resulted in chloroform increases of up to 20 times the original concentration. Laboratory and field experiments at a bleached kraft mill indicate that the magnitude of chloroform generated through this process will depend on the specific bleaching conditions in the chlorination stage and on the pH of the combined mill sewer. In some cases, this effect may account for a significant fraction of the chloroform in the influent to wastewater treatment system.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
40.	Influence Of Chlorine Ratio And Oxygen Bleaching On The Formation Of PCDFs And PCDDs In Pulp Bleaching, Part 1: A Laboratory Study	de Sousa, F.; Kolar, M.-C.; Kringstad, K.P.; Swanson, S.E., Rappe, C.; Glas, B.	TAPPI Journal, April 1989, pp. 147-152.	In a laboratory bleaching study, we assessed the influence of the chlorine ratio and oxygen bleaching on the amounts of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxin (PCDDs) formed. A significant factor affecting the amounts of PCDF and PCDD is the chlorine ratio. On well-washed laboratory pulp, oxygen bleaching has little or no effect, The beneficial effects of oxygen bleaching on the amounts of PCDFs and PCDDs observed in mill-scale studies is therefore likely the result of the much greater efficiency in pulp washing through the oxygen bleaching stage.
41.	Worldwide E Installations Survey, A	Reeve, D.W.	TAPPI Journal, November 1985, pp. 142-143.	World wide survey of Eo (use of oxygen in the extraction stage of chemical pulp bleaching) installations.
42.	Fraternity Gathers at the Chateau: The 1985 International Pulp Bleaching Conference	Pryke, D.C.	TAPPI Journal, August 1985, pp. 145-147.	Overview of general subjects discussed during the conference. Major topics were chlorine-free processes, importance of mixing, oxidation extraction, chlorine dioxide bleaching, and the future of bleaching.
43.	Delignifying High-Yield Pulps With Oxygen and Alkali	Kleppe, P.J.; Storebraten S.	TAPPI Journal, July 1985, pp. 68-73.	Discussion of delignifying high-yield pulps with oxygen and alkali by using a two stage pulping process. Pulp properties, sack paper production and linerboard production are discussed.
44.	Paper Industry Consumption of ClO2 Soars as Available Supply Tightens	Downs, T., Technical Editor	Pulp & Paper, October 1989, pp. 111-112.	Article discusses trend toward high chlorine dioxide substitution, anticipated supply problems and part this substitution plays in meeting anticipated requirements.
45.	The Future of Bleaching	Reeve, D.W.	TAPPI Journal, June 1985, pp. 34-37.	Summary of what is taking place in bleaching, what are the economic influences and what is predicted to happen in the near future.
46.	Chlorinated Organic Matter in Bleached Chemical Pulp Production: Part III -The effect of Chlorination Stage Variables on Chlorinated Organic Matter in Effluents	Earl, P.F.; Reeve, D.W.	TAPPI Journal, October 1989, pp. 183-187.	Softwood kraft pulps were chlorinated at low and medium consistency in the laboratory, covering a wide range of chlorination levels, with and without chlorine dioxide substitution. The filtrates from the chlorination and extraction stages were analyzed for AOX and EOX. AOX formation decreased when mixing was improved, but EOX was unchanged. At 50% ClO2 substitution AOX formation fell by 40%. Equations were developed to estimate the amount of AOX and EOX formed, based on the elemental chlorine in the oxidant consumed by the pulp.
47.	Chlorinated Organic Matter in Bleached Chemical Pulp Production: Part VI - Chlorinated Compounds in Effluents	Earl, P.F.; Reeve, D.W.	TAPPI Journal, January 1990, pp. 179-184.	Fifty percent ClO2 substitution significantly decreased the total amount of chlorinated phenolic compounds and the amount of tetrachlorinated phenolic compounds in chlorination and extraction stage effluents. Improved chlorination stage mixing also decreased the formation of tetrachlorinated phenolic compounds significantly. Chloroform formation in the chlorination stage was decreased by improved mixing, by increased consistency and by 50% ClO2 substitution.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
48.	Eo Installations Survey	Reeve, D.W.	TAPPI Journal, October 1984, pp. 110-111.	World wide summary of oxygen delignification (EO), processes installed. Dramatic growth in EO installations is reported.
49.	Oxygen Delignification Systems: Optimum Design Syntheses	Edwards, L.; Myer, M.; Haynes, J.	TAPPI Seminar Proceedings, Bleaching and the Environment, Seattle, Washington, September 1988, pp. 333-356.	Simulation and optimization techniques are used to determine the best combination of equipment and operating conditions from an oxygen delignification system including washing. Both capital costs and operating costs are considered. For example, "What is the optimum dilution factor and amount of washing equipment and how should the equipment be divided between pre- and post-oxygen stage washing?" Evaporator and environmental constraints are also taken into account.
50.	Oxidative Extraction at Halsey Mill Cuts Hypochlorite Consumption	Ducey, M.J., Technical Editor	Pulp & Paper, October 1984, pp. 118-119.	Discussion of how an Oxidative Extraction System having a high-shear mechanical mixer repaid its capital costs within one year. System installation considered a success.
51.	Some Bleach Plant Modification To Reduce The Amount Of Toxic Substances In Pulp And Filtrate	Edwards, L.; Myers, M.; McKean, B.	TAPPI Seminar Proceedings, Bleaching and the Environment, Seattle, Washington, September 1988, pp. 328-332.	This report discusses the benefits of increasing the amount of lignin removed from the brownstock pulp through more efficient washing.
52.	Consultants View On The European Environmental Requirements And Enforcement Activities Related To Aqueous Discharges From The Pulp And Paper Industry, A	Folke, J.		Cooperation on environmental issues in Europe is performed by means of more than 20 organizational bodies ranging from well-known international organizations to a number of conventions ratified individually by state governments. This paper discusses some of the problems that have to be considered when issuing wastewater discharge permits to the pulp and paper industry, including the choice of parameters to regulate the discharge of chlorinated matter and dioxins, chemical balances in pulp bleaching, and the question of energy, entropy and environmental protection.
53.	Tutorial - Non-chlorine Bleaching Of Chemical Pulp	Liebergott, N.; van Lierop, B.; Garner, B.C.; Kubes, G.J.	TAPPI Proceedings, 1987 Environmental Conference, pp. 303-312.	Two bleaching sequences were developed for a kraft pulp (kappa # 30.6) that avoid chlorine-containing compounds by using only oxygen (O), ozone (Z), sodium hydroxide (E), hydrogen peroxide (P) and sodium hydrosulphite (Y). Effluents were 40-60% lower in colour than those obtained from a conventional C/DEDED sequence. The oxygen stage may be done at medium (7%) or high (25%) consistency. After the sequence OZEP, the pulps had a brightness of 80-86% ISO. In the sequence ZOP, the final brightness could be improved by 10 points if the ZO bleached pulps were washed with effluent from the Z stage. Semi-bleached pulps from both sequences achieved a brightness of 88-90% on final-stage bleaching with hydrosulphite. The strength properties of pulps bleached by these novel sequences and by conventional C/DEDED, OZEPY and ZOPY sequences was evaluated.

ATTACHMENT A - REFERENCES
TECHNOLOGIES FOR THE CONTROL AND REDUCTION OF CHLORINATED ORGANICS FOR THE PULP INDUSTRY

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
54.	Pretreatment Of Kraft Pulp Is The Key To Easy Final Bleaching	Fossum, G.; Marklund, A.	TAPPI Journal, November 1988, pp. 79-84.	Low values of total organic chlorine (0.5 kg/metric ton) were reached with a combination of extended delignification to kappa numbers below 10 and a high chlorine dioxide fraction in the prebleaching.
55.	Final Bleaching of Kraft Pulps Delignified to Low Kappa Number by Oxygen Bleaching	Fossum, G.; Lindqvist, B.; Persson, L.-E.	TAPPI Journal, December 1983, pp. 60-62.	Discussing of pretreatment kraft pulp with nitrogen dioxide and oxygen prior to oxygen bleaching, Chemical demand, pulp viscosity, strength and yield and bleach effluents from pretreated sequence is compared to conventional oxygen bleaching.
56.	How Bleaching Hardwood Kraft Pulp with Oxygen Affects the Environment	Jones, A.R.	TAPPI Journal, December 1983, pp. 42-43.	Article provides short explanation of conventional and oxygen bleaching sequences and compares effluent volume, color and BOD from the two processes.
57.	Short Sequence Bleaching with Oxygen: Part II	Schleinkofer, R.W.	TAPPI Proceedings, 1982 Pulping Conference, pp. 303-308.	Laboratory bleaching data from the sequences C/D-E-D-E-D, O-C/D-E-D, C/D-E-Eo-D, O-C/D-Eo-D, and C/D-Eo-D-E-D are compared for two softwood kraft pulps. Costs, Kappa No., viscosity, brightness, energy consumption, and effluent properties are compared.
58.	Automated ClO2 Generation Improves Bleaching, Cuts Effluent	Evans, J.C.W., Senior Editor	Pulp & Paper, February 1983, pp. 69-71.	Discussion of continuous monitoring and control for a chlorine dioxide generator.
59.	Technical Consequences of New Knowledge on Prebleaching with a High Fraction of Chlorine Dioxide	Germgard, U.	TAPPI Journal, December 1982, pp. 81-83.	Prebleaching of softwood kraft pulp with chlorine dioxide and low fraction of chlorine has been studied in the laboratory under well-controlled bleaching conditions. This paper concentrates on the influence of the chlorine fraction and of a preceding oxygen bleaching stage. The technical consequences are discussed, particularly for the case where an oxygen bleaching stage precedes a pure chlorine dioxide prebleaching stage.
60.	Oxygen Bleaching System Operating Well at Union Camp's Franklin Mill	Smith, K.E., Executive Editor	Pulp & Paper, October 1982, pp. 90-93.	Overview of oxygen bleaching system at Union Camp's Franklin mill. Process is a four stage OC/DED sequence reporting a reduced chemical and water usage and improved effluent treatment.
61.	Bleaching Technology Review: Recent Developments, Future Treads	Macleod, M.	Pulp & Paper, October 1982, pp. 61-65.	Discussion of chlorination issues, chlorine free bleaching, sequence modifications, optimizing sequences without oxygen and displacement bleaching, and closed cycle systems. Total organic chloride generated by various sequences is presented.
62.	Relative Rates of Consumption of Chlorine and Chlorine Dioxide During (D + C) Bleaching of Softwood Kraft Pulp, The	Germgard, U.; Teder, A.; Tormund, D.	TAPPI Journal, May 1982, pp. 124-126.	Experiment presenting the relationship between consumption of chlorine dioxide and chlorine during (D&C) bleaching.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
63.	Short Sequence Bleaching With Oxygen: Part I	Schleinkofer, R.W.	Pulp & Paper Canada, 83:11 (1982)	Two unbleached kraft pulp samples, one hardwood and one softwood, produced by two eastern Canadian mills, were bleached in the laboratory by the sequences C/DEDED, OC/DED and OC/DEoD. Fully bleached pulps of 90 ISO brightness were obtained with the sequence OC/DEoD at substantial savings in chemical cost compared to sequence C/DEDED, and strength properties were almost identical. Energy balances show very small differences in net steam and power demand.
64.	Oxygen Delignification Technology: State-of-the-Art Report on Advances	White, F.	Paper Trade Journal, February 28, 1982, pp. 27-30.	Oxygen and ozone delignification in the bleaching of kraft pulps are compared. Medium consistency oxygen delignification of kraft pulp is described. Aspects of low cost peroxide bleaching to high brightness are covered, and hydrogen peroxide in chemical pulp bleaching is discussed.
65.	System Using Medium-Consistency Oxygen Bleaching Works in Sweden, A	Nasman, L.E.	Pulp & Paper, October 1981, pp. 137-138.	SCA mill at Ostrand has successfully run a full-scale oxygen-caustic extraction stage. The advantages of oxygen plus oxygen-extraction stage are described.
66.	Oxygen Delignification at Medium Consistency Can Raise Yield, Cut BOD	Markham, L.D.; Magnotta, V.L.	Pulp & Paper, October 1981, pp. 139-142.	General discussion of oxygen delignification including advantages and disadvantages, process, pulp yield and effluent reduction.
67.	Investigation for Presence of PCDDs and PCDFs in Bleaching Process from Pulp & Paper Industries	Fouquet, A.; et al.	Dioxin '89, September 1989	
68.	Developments in Chlorine Dioxide Bleaching	Reeve, D.W.; Rapson, W.H.	TAPPI Journal, September 1981, pp. 141-143.	Discussion of increased replacement of chlorine by chlorine dioxide in the first stage, Dc-C serial bleaching, and chlorine in chlorine dioxide bleaching. A comparison of bleaching sequences with respect to chemical usage, energy required, and inflation of chemical and energy costs is provided.
69.	New Opportunities for In-Plant Reduction of Pollutants Through Process Changes	Renard, J.J.; Phillips, R.B.; Jameel, H.; Rudie, A.W.	TAPPI Journal, August 1981. pp. 51-54.	Four process options- medium-consistency oxygen delignification, low-kappa-number kraft/AQ pulping, chlorine dioxide substitution, and caustic extraction in the presence of oxygen (Eo stage) - were compared in terms of production cost, environmental impact, and product quality. The oxygen-based options were identified as the most cost effective options to reduce the pollution load of a bleached kraft mill through process modification.
70.	Oxygen/Alkali Delignification at Medium Consistency	Kleppe, P.J.; Knutsen, P.C.; Jacobsen, F.	TAPPI Journal, June 1981, pp. 87-90.	The sequence of events leading to the development of a mill-scale oxygen/alkali delignification process at medium consistency is described. The process, which takes pulp directly from the blow line of a continuous digester, is also presented. The mill in the M. Peterson & Son mill in Moss, Norway.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
71.	Evaluation of Measures to Control Chlorinated Dioxin and Furan Formation and Release at Bleached Chemical Pulp Mills, An	Halliburton, D.; Chung, A.	Dioxin '89, September 1989	
72.	Kraft Mill Bleach Plant Effluents: Recent Developments Aimed At Decreasing Their Environmental Impact, Part 1	Heimburger, S.A.; Blevins, D.S.; Bostwick, J.H.; Donnini, G.P.	TAPPI Journal, October 1988, pp. 51-59.	A review of developments in the technology of pulping and bleaching has demonstrated new ways to decrease the formation of chlorinated organic materials. A review of the composition of bleach plant effluents and at effluent treatment methods was also studied.
73.	Kraft Mill Bleach Plant Effluents: Recent Developments Aimed At Decreasing Their Environmental Impact, Part 2	Heimburger, S.A.; Blevins, D.S.; Bostwick, J.H.; Donnini, G.P.	TAPPI Journal, November 1988, pp. 69-78.	In Part 1, processes that reduce the chemical demand of pulp by lowering the kappa number prior to bleaching were investigated. These methods included extended delignification and oxygen delignification. In Part 2, other approaches such as chlorine dioxide substitution, oxygen extraction, hydrogen peroxide reinforcement, ozone and alternative bleach schemes without chlorine are examined. Treatment methods including biological and physical/chemical are also investigated.
74.	Medium-Consistency Oxygen Bleaching - An Alternative to the High-Consistency Process	Nasman, L.E. ; Annergren, G.E.	TAPPI Journal, April 1980.	Medium-consistency oxygen bleaching has been examined both in the laboratory and on a pilot-plant scale and has been found to give very encouraging results in terms of delignification and chemical consumption. Discussion of the laboratory and pilot plant studies and commercial application is provided.
75.	Oxygen Bleaching Shows Potential for Reducing Costs and Effluent Problems	Chang, H.-M.	Pulp & Paper, March 1980, pp. 87-91.	Discussion of the oxygen bleaching process, advantages and disadvantages, new processes being implemented, dissolved oxygen displacement delignification process (DODEL), and low- and medium-consistency oxygen bleaching.
76.	Oxygen Bleaching Shows Potential For Reducing Costs, Effluent Problems	Almberg, L.; Jamieson, A.; Waldestam, S.	Pulp & Paper, March 1980, pp. 92-95.	Capital and operating costs, energy consumption, and degree of pollutant reduction are compared for oxygen bleaching and biological treatment.
77.	Chlorinated Organic Compounds In Effluent Treatment At Kraft Mills	Gergov, M.; Priha, M.; Talka, E.; Valttila, O.; Kangas, A.	TAPPI Proceedings, 1988 Environmental Conference, Charleston SC, April 1988, pp. 443-455.	The formation of chlorinated organic compounds and their behavior in effluent treatment were studied for softwood and hardwood pulping at two kraft mills, one modern with five-stage bleaching and an activated sludge plant, the other a conventional mill with six-stage bleaching and an aerated lagoon. Total organically bound chlorine, chlorophenolics, volatile chlorine compounds and chloroacetones were determined in bleach plant effluents and at different stages of effluent treatment.
78.	Handbook for Pulp & Paper Technologists	Smook, G.A.; Kocurek, M.J.	Canadian Pulp & Paper Association and TAPPI, 1989 Edition.	See Title.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
79.	Mill Experience With Oxygen And Hydrogen Peroxide Bleaching Stages	Helmling, O.; Suess, H.U.; Meier, J.; Berger, M.	TAPPI Journal, July 1989, pp. 55-61.	Discussion of using hydrogen peroxide in both delignification and extraction stages of bleaching and of reinforcing stages with oxygen and hydrogen peroxide. Reinforcing the EO stage with hydrogen peroxide (EOP) is economical and gives better pulp qualities. EOP can be used efficiently as a first bleaching stage in sulfite pulp mills.
80.	Design, Startup and Operating Experience for an Expanded ASB Treatment System at Champion's Pensacola Mill	Hilleke, J.; Koelsch, S.; Arceneaux, D.	TAPPI Journal, September 1989, pp. 111-117.	In December 1986, Champion completed the conversion of its Pensacola kraft mill to 100% bleached pulp and paper operation. New pine and hardwood bleach lines were set up, along with an oxygen delignification sequence. To successfully operate the converted mill in compliance with new permit conditions, the project included major modifications to the waste treatment system
81.	Formation of Chlorinated Dioxins and Furans from Lignin and Lignin Model Compounds	Hise, R.G.	Dioxin '89, September 1989	
82.	Split Addition of Chlorine and pH Control for Reducing Formation of Dioxins	Hise, R.G.	TAPPI Journal, December 1989, pp. 121-126.	Process modifications in the chlorination stage produce high brightness, high viscosity pulps with dramatically reduced levels of 2378-TCDD and 2378-TCDF, and can be implemented faster and more economically than other techniques.
83.	Effects Of Oxygen Extraction On Organic Chlorine Contents In Bleach Plant Effluents	Hong, Q.; Shin, N.H.; Chang, H.-M.	TAPPI Journal, June 1989, pp 157-162.	An unbleached kraft pulp and an oxygen-prebleached kraft pulp were chlorinated at various chlorine dosages. The chlorinated pulps were extracted under conditions for alkaline extraction (E) and oxygen-alkali extraction (EO). The organic chlorine (OCl) in the pulps and in the spent liquors from each stage were determined, to study the effect of EO on OCl emission. EO alone had little effect on the OCl emission, but EO combined with oxygen prebleaching was more effective in reducing the OCl in both the spent liquor and in the pulp than a conventional extraction stage (E). Chlorination of oxygen-prebleached pulp involves more oxidation and less substitution than chlorination of nonoxygen-delignified pulps. The EO stage is more efficient in converting the OCl to chloride. An EO stage can further reduce the OCl discharge by lowering the requirement for chlorine.
84.	Pilot Plant Trials For LRP, A New Process For Precipitating Organic Material	Hynninen, P.	TAPPI Journal, February 1989, pp. 167-170.	The lignin removal process (LRP) is a new method for precipitating dissolved or colloidal organic material of high molecular mass from fibrous waste sludge. Effluents successfully treated have been taken from bleaching plants, barking rooms and fiberboard mills from white water systems of some paper and fiberboard mills and from CTMP mills. Pilot plant trials at a kraft pulp mill and at a fiberboard mill produced results similar to those obtained by chemical precipitation and by the previous laboratory tests. The pilot plant results support ideas for the design of LRP effluent treatment plants. LRP is simple and inexpensive to incorporate into existing mechanical and biological treatment and the method is ready for industrial use.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
85.	Reduction of Chloro-organic Discharge in the Nordic Pulp Industry	Jaakko Poyry		The report examines available technical measures and their economic consequences aimed at the reduction of the discharge of chlorinated organic materials from the Nordic pulp industry.
86.	AOX Testing Of Bleach Plant Effluents	Johannes, D.L.		Although there are no limits on AOX (adsorbable organic halogen) on current bleach plant effluents in North America, recent government actions and public opinion concerning chlorinated bleach effluents may require mills to monitor their effluents on a regular basis for AOX and other components. A description of the AOX determination and associated good laboratory procedures will be given. A summary of some lab work on reducing AOX will be included.
87.	Modified Continuous Kraft Pulping-Now A Reality	Johansson, B.; Mjoberg, J.; Sandstrom, P.; Teder, A.	Svensk Papperstidning, 10, 30(1984).	Full scale mill trials have been carried out in Varkaus, Finland with modified continuous draft cooking in cooperation between Ahlstrom, Kamyr and STFI. The process is characterized by a low initial concentration of alkali and by low concentrations of lignin and sodium ions towards the end of the cook. The process gives several advantages compared to the conventional one such as improved pulp strength, better bleachability, lower variable costs and decreased environmental load.
88.	Ultrafiltration Of Bleach Plant Effluent	Jonsson, A.-S.	Nordic Pulp and Paper Research Journal, 1-1987, 23-29.	An up-to-date evaluation of capacity and retention of new membranes with regard to bleach plant effluents has been made. The results from a trial of seven reverse osmosis, ultrafiltration and microfiltration membranes are reported. The trial has even included membranes not yet commercially available. The trial has demonstrated that some of the tested membranes could probably combine a satisfactory flux and an acceptable retention. A rough estimate of the costs shows that treatment of the E-stage effluent with ultrafiltration could be performed within a total cost of approximately 25 SEK per tonne of pulp.
89.	Experience With Extended Delignification Of Hardwood And Softwood Kraft Pulp In A Continuous Digester	Kortelainen, V.A.; Backlund, B.A.	TAPPI Journal, November 1985, pp. 70-74.	A multistage continuous kraft pulping process that provides a more selective delignification than conventional kraft cooking is in commercial operation at a mill in Finland. This improved selectivity is used to lower the pulp's kappa number, which has contributed to reductions in the consumption of bleaching chemicals, to reductions in the effluent load of the bleach plant, and to an increase in the bleach plant's production capacity. When compared at the same kappa number, the modified pulp has a higher viscosity, better strength and consumes less bleaching chemicals than a conventional kraft pulp. Operating experiences, consumption data and pulp-quality data for hardwood and softwood kraft pulps are reported.
90.	Bleaching And The Environment	Kringstad, K.P.; de Sousa, F.; Johansson, L.; Kolar, M.-C.; Swanson, S.E.	Addendum to paper presented at the TAPPI/CPPA 1988 International Pulp Bleaching Conference, Orlando, Florida, June 1988.	Paper discusses the formation of dioxins in the kraft bleaching process and measures to decrease or eliminated such formation.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
91.	Influence Of Chlorine Ratio And Oxygen Bleaching On The Formation Of PCDFs And PCDDs In Pulp Bleaching, The, Part 2: A Full Mill Study	Kringstad, K.P.; Johansson, L.; Kolar, M.-C.; de Sousa, F.; Swanson, S.E.; Glas, B.; Rappe, C.	TAPPI Journal, June 1989, pp.163-170.	We studied the effect of low-chlorine bleaching on the formation of polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins (PCDFs and PCDDs) in full mill-scale experiments. An oxygen-bleached softwood kraft pulp with a kappa number of 19.5 was bleached using 33.3 kg of Cl2 and 6.2 kg of ClO2 per ton of pulp in the first stage. A similar pulp was bleached using a mixture of 19.3 kg Cl2 and 12.5 ClO2 per ton to pulp. The amounts of PCDF and PCDD dropped strongly in bleaching at the low chlorine ratio. the concentration of PCDFs and PCDDs in general was only slightly above the detection limits in the pulp as well as in the total effluent. These results confirm those of the laboratory study (Part 1) which suggested that the chlorine ratio used in the first bleaching stage is important in the formation of PCDFs and PCDDs.
92.	Spent Liquors From Pulp Bleaching	Kringstad, K.P.; Lindstrom, K.	Environmental Science & Technology, 18(8), 236A(1984).	Impact of chlorination and extraction stage variables on formation of chlorinated organics.
93.	Bleaching And The Environment	Kringstad, K.P.; McKague, A.B.	TAPPI/CPPA Proceedings, 1988 International Pulp Bleaching Conference, Orlando, Florida, June 1988.	Combinations of treatment of effluents in aerated lagoon, the use of oxygen bleaching, the partial replacement of chlorine by chlorine dioxide and/or applying low chlorine ratio bleaching in combination with reinforced alkaline extraction may yield effluents: which meet advanced requirements regarding protection of fish and other organisms living in pulp mill receiving waters against toxic effects and according to all present knowledge reduce chances of any widely spread detrimental environmental effects of chlorinated organic materials.
94.	Studies on the Mechanism of PCDD/PCDF Formation during the Bleaching of Pulp	LaFleur, L.E.; et al.	Dioxin '89, September 1989	
95.	Oxygen Bleaching, Today's Standard For Pollution Abatement - PRENOX Next To Come?	Lindblad, P.; Norden, S.	The Fifth Technical Seminar at Sunds Defibrator Proceedings, Sundsvall, June 1988.	Paper discusses modified cooking, oxygen delignification and PRENOX. Information is presented related to kappa numbers, AOX, TOCl and costs.
96.	Nitrogen Dioxide Preoxidation Oxygen Delignification - A Process For The Future?	Lindqvist, B.; Marklund, A.; Lindstrom, L.-A.; Norden, S.	TAPPI Proceedings, 1985 International Pulp Bleaching Conference, pp. 221-225.	In order to produce a low kappa number pulp after an oxygen stage nitrogen dioxide preoxidation was superior to modification of the kraft cook, kappa number 9-10 should be compared to 13-14 in the latter case. A number of these methods made it possible to further reduce the kappa number to about 8 after the oxygen stage. Kappa number reduction from 17 to 9, the first figure representing a conventionally cooked and oxygen bleached kraft pulp, decreased the consumption of active chlorine up to 55%. COD, BOD7 and total organic chlorine were reduced with 55%, while color was reduced with 75%.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
97.	Selective Removal Of Chlorinated Organics From Kraft Mill Total Effluents In Aerated Lagoons	Lindstrom, K.; Mohamed, M.	Nordic Pulp and Paper Research Journal No. 1/1988, pp. 26-33.	The efficiency of aerated lagoon in reducing the quantity of various chlorinated organics occurring in kraft pulp mill total effluent was assessed. The most abundant chlorinated neutrals, phenols and acids so far identified, as well as the non-volatile organochlorine in the influent and effluent to the lagoon were measured by methods earlier established. The most efficient removal was observed for the most abundant chlorinated compounds occurring in the waste water (chlorinated acetic acids and chloroform). Among the chlorinated organics studies, DDS (1,1-dichlorodimethyl sulfone) was apparently the least affected by aerated lagoon treatment. Extended retention period in lagoons from 2.5 to 5 days had almost quantitatively removed the acids, particularly trichloroacetic acid.
98.	Oxygen Delignification Systems: Synthesizing the Optimum Design	Myers, M.; Edwards, L.; Haynes, J.	TAPPI Journal, April 1989, pp. 131-135.	The authors used computer simulation to synthesize the best configuration of washing equipment and determine the optimum dilution factor for a typical oxygen delignification system.
99.	Chlorinated Organic Matter In Bleached Chemical Pulp Production Part II: Measurement Techniques For Effluents	Odendahl, S.M.; Weishar, K.M.; Reeve, D.W.	Presented at the CPPA Technical Section Annual Meeting, January 31-February 3, 1989.	Quantification of the chlorinated organic matter discharged from chemical pulp bleach plants is becoming an important part of harmonizing operations with the environment. AOX (adsorbable organic halogen) measurement involves adsorption of all organic matter onto activated carbon, mineralization by combustion forming HCl, and then determination of chloride. The principles and details of AOX techniques and AOX instruments are described.
100.	Survey of Chlorine Dioxide Generation in the United States, A	Owen, D.; Perot, P.; Harrington, E.; Scribner, H.C.	TAPPI Journal, November 1989, pp. 87-92.	There is plenty of room for improvement in the processes used to produce chlorine dioxide. With its impact on the environment and bleaching costs, mills will spend more time reviewing the operations of their chlorine dioxide generation plants.
101.	Direct Biological Bleaching of Hardwood Kraft Pulp with the Fungus Corioius Versicolor	Paice, M.C.; Jurasek, L.; Ho, R.; Bourbonnais, R.; Archibald, F.	TAPPI Journal, May 1989, pp. 217-221.	Researchers at PAPRICAN screened various microorganisms and found that Coriolus versicolor can bleach hardwood kraft pulp by up to 15 percentage points with a drop in kappa number from 11.6 to 7.9. The bleaching effect of C. versicolor appears to be limited to hardwoods since experiments with spruce pulp failed to increase brightness.
102.	Dechlorination Of High-molecular-weight Chlorolignin By The White-rot Fungus *P. Chrysosporium*	Pellinen, J.; Joyce, T.W.; Chang, H.-M.	TAPPI Journal, September 1988, pp. 191-194.	Dechlorination of chlorolignin in pulp bleaching wastewater was studied using the white-rot fungus *P. chrysosporium* immobilized on a rotating biological contactor. The total organic chlorine content of chlorolignin decreased almost by 50% during one day of treatment. The corresponding amount of inorganic chloride was liberated into the solution. Correlation studies suggested that dechlorination, decolorization, and degradation of chlorolignin (as COD decrease) are metabolically connected, although these processes have different rates. Size exclusion chromatography showed that polymerization took place in the early stage of the treatment. Low-molecular weight degradation products were not observed.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
103.	Substituting Chlorine Dioxide for Chlorine	Pryke, D.C.	TAPPI Journal, October 1989, pp. 147-155.	Increasing chlorine dioxide substitution minimizes bleaching chemical consumption, decreases costs, and improves effluent quality.
104.	Chlorination-stage Mixing Practices	Pryke, D.C.	TAPPI Journal, June 1989, pp. 143-149.	Examples of mill chlorination stages show that many process and equipment choices are available to meet the environmental, economic, and process demands of the modern bleach plant.
105.	Chlorinated Organic Matter In Bleached Chemical Pulp Production: Part I - Environmental Impact And Regulation Of Effluents	Reeve, D.W.; Earl, P.F.	Pulp & Paper Canada, 90(4): 65(1989).	In two recent Swedish studies, bleach plant effluents have been found to have significant environmental impact even after extreme dilution. These findings are contrary to earlier Swedish work and to North American experience but have nonetheless led to regulations in Sweden requiring decreasing discharge to as low as 1.5 kg TOCl (total organic chlorine) per tonne of pulp, 25% of the amount discharged from conventional bleaching of softwood kraft pulp.
106.	Modified Kraft Cooking - Ways Of Application	Sandstrom, P.E.; Parming, A.M.; Soderqvist Lindblad, M.; Teder, A.	TAPPI Seminar Proceedings, Bleaching and the Environment, Seattle, Washington, September 1988, pp. 279-286.	Modified kraft cooking is based on principles that originate from the kinetics of delignification and carbohydrate degradation. Some of the principles contradict others, so it is therefore necessary to optimize process conditions to gain a net improvement in pulping selectivity. This paper presents how different ways of applying the principles can be evaluated using a mathematical model of continuous kraft pulping. Mill trials and laboratory investigations show that correctly applied, the principles result in a process that both reduces bleach plant effluent and operating costs while maintaining the pulp quality. The modified kraft cooking process can probably be even further improved based on advancing knowledge in the field of pulping chemistry.
107.	Formation Of Chlorinated Lignin Products	Sarkanen, K.V.	TAPPI Seminar Proceedings, Bleaching and the Environment, Seattle, Washington, September 1988, pp. 313-327.	Paper discusses the 1) chemistry of formation of chlorinated lignin products such as chlorolignin, chlorinated guaiacols, catechols, phenols, vanillins, chlorinated aliphatics, chloroform and methanol and 2) the potential formation of PCDDs and PCDFs from lignin.
108.	Effects of Brownstock Washing on the Formation of Chlorinated Dioxins and Furans During Bleaching, The	Hise, R.G.; Hintz, H.L.	TAPPI Journal, January 1990, pp. 185-190.	Poor brownstock washing led to increased levels of PCDDs and PCDFs in softwood pulps after chlorination stage and in the final effluent. Additional washing in the laboratory with copious amounts of aqueous ethanol decreased chlorinated dioxins and furans by 80%. These results demonstrate the presence of solvent-extractable precursors for PCDD/Fs associated with this unbleached pulp. Also found that spiking unbleached pulp with higher than normal levels of defoamers used had no significant effect on the formation of PCDD/Fs after bleaching.
109.	The Impact Of Environmental Concern On The Future Of Chemical Pulping And Bleaching	Silander, R.	International Seminar at Sunds Defibrator AB, 1988.	Paper discusses evolution of environmental regulations and their impact on production processes for the 1990's.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
110.	Two Case Studies On The Cold Blow Technique For Batch Kraft Pulping	Sjodin, L.; Pettersson, B.	TAPPI Journal, February 1987, pp. 72-76.	The ASSI Karlsborg mill is the first to practice extended delignification and cold blow process techniques in its batch digester plant, and the NCB Dynes mill started up a completely new batch cold blow digester plant recently.
111.	Operational Experiences From A New Chlorination Control System Based On On-line Measurements Of Kappa Number	Soderberg, J.; Almberg, M.; Kubulnieks, E.; Lundqvist, S.-O.; Lowenberg, C.	TAPPI Journal, November 1988, pp. 145-149.	In a new control system for chlorination, the change of active chlorine is based on on-line measurement of the kappa number of the pulp entering the bleach plant. The control system also accounts for variations in production, temperature, etc. The kappa number after the alkali extraction stage is also measured on-line. The control system is installed in a bleach plant for softwood kraft pulp, where the residual chlorine has been reduced by 3 kg Cl/ton of pulp, the quantity of downgraded pulp has decreased, and the working conditions have improved. The control system is flexible during operation under various bleaching conditions.
112.	Personal communication between D. G. Bodien of EPA and V.E. Lennon, Jr. of Ingersoll-Rand Company	Ingersoll-Rand Company		Communication contains information related to costs related to compaction baffle filters and oxygen delignification systems.
113.	Determination of Total Organic Chlorine in Pulp	Stevens, B.; Sell, L.O.; Easty, D.B.	TAPPI Journal, July 1989, pp. 181-182.	Analytical method for TOCl in pulp described.
114.	Rapid Displacement Heating in Batch Digesters	Swift, L.K.; Dayton, J.S.	Pulp & Paper Canada, 89:8, pp. T264-T270.	Rapid Displacement Heating (RDH) has now reached full commercial operation in two mills. In addition to dramatic digester area steam savings these mills have experienced reduced soda loss off brown stock washers; reduced evaporator load; lower strong black liquor viscosities; increased digester production and improved pulp quality.
115.	Advances in Bleach Plant Design Lower Capital and Operating Costs	Tait, D.H.	Pulp & Paper, January 1986, pp. 70-72.	Improved washing and mixing technologies reduce chemical consumption without offsetting power usage and effluent increases.
116.	Personal communications between D. G. Bodien of EPA and A. Melin of Statens Naturvårdsverk	Statens Naturvårdsverk		Communications contains information related to oxygen delignification, extended delignification, biological treatment at Swedish kraft pulp mills. Also contains removal efficiencies for ultrafiltration facility at MoDoCell Husum mill.
117.	Membrane Filtration As A Technique For Effluent Control In Pulp And Papermaking	Thorsell, L.; Orchard, T.	TAPPI Seminar Proceedings, Bleaching and the Environment, Seattle, Washington, September 1988, pp. 227-243.	Paper presents information related to membrane filtration (ultrafiltration and reverse osmosis). Applications, installations and costs are presented.
118.	Bleaching of Kraft Pulp Without Formation of Dioxins	Vaheri, M.; et al.	Dioxin '89, September 1989	

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
119.	Some New Insights Into The Origins Of Dioxins Formed During Chemical Pulp Bleaching	Voss, R.H.; Luthe, C.E.; Fleming, B.I.; Berry, R.M.; Allen, L.H.	Paper presented at the 1988 CPPA Environment Conference, Vancouver, B.C., October 25-26, 1988.	Oil-based pulp mill additives, particularly brownstock defoamers, have been identified as potential sources of unchlorinated furan (DBF) and dioxin (DBD) which can be converted to their chlorinated forms in the chlorination stage of pulp bleaching. To get a clean indication of the effect of defoamers on the formation of chlorinated dioxins and furans (together commonly referred to as dioxins), a higher than normal defoamer charge (1% by weight on o.d. pulp) was used for these preliminary experiments. Subsequent studies in our laboratory have established that DBF-contaminated defoamers even when applied at normal industrial charges (i.e., 0.1 to 0.3%) were able to cause significant increases in the dioxin content of the final chlorinated pulp.
120.	Dioxin/Furan In-Mill Source Studies at Consolidated Papers, Inc.'s Kraft Division	Weinbauer, J.; Gilbert, F.A.	TAPPI Proceedings, 1989 Environmental Conference, April 1989, pp. 359-372.	Impact of oxygen delignification on hardwood bleach line reviewed.
121.	Industry's Effluent Problems Spawn New Engineering Technology, Design	Galloway, L.R.; Helminen, P.I.; Carter, D.N.	Pulp & Paper, September 1989, pp. 91-97.	Article reviews development of environmental regulations for Sweden, Canada and U.S.. Also reviewed are inplant and external technologies installed to reduce the discharge of chlorinated organics. These include extended delignification, oxygen delignification, advanced pulp washing, ClO2 substitution, reduced water usage and biological wastewater treatment.
122.	STFI OPTI-Kappa Analyzer, Application and Accuracy	Kubulnieks, E.; Lundqvist, S.-O.; Pattersson, T.	TAPPI Journal, November 1987, pp. 38-42.	STFI has developed an on-line kappa number measurement system based on absorption of ultraviolet light. This measurement system is now a well-established systems which has been in operation in different applications for more than three years in Swedish mills. The operating experiences are good, with low maintenance and, in most cases, almost 100% availability.
123.	Kraft Mill Effluents in Ontario	Bonsor, N.; McCubbin, N.; Sprague, J.B.	Technical Advisor Committee, Pulp & Paper Sector of MISA, Ontario Ministry of the Environment, Toronto, Ontario, Canada, April 1988.	This report reviews the effluent discharged by the kraft pulp industry in Ontario, and recommends a water pollution control strategy. The recommendations are based on the needs of the aquatic ecosystem, current technology, water pollution control practices in other kraft pulp producing jurisdictions, and economic factors.
124.	Alternate Process for Bleaching Could Help in Reducing TOCls, Dioxin	Galluch, R.J.	Pulp & Paper, September 1989, pp. 145-147.	Monox-L technology, successful in five plant trials, maintains pulp quality similar to that produced with chlorine dioxide.
125.	New Flocculation Process Portends Progress in Color, Dioxin Removal	Mass, R.P.; Neal, J.P.	Pulp & Paper, September 1989, pp. 154-158.	Article discusses how Hansel process removed 90 to 95 percent of lignin, tannins, and dioxin from secondary treated bleached kraft mill wastewater.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
126.	USEPA/Paper Industry Cooperative Dioxin Study: The 104 Mill Study (Preliminary Results)	Whittemore, R.C.; LaFleur, L.E.; Gillespie, W.J.; Amendola, G.A.; Helms, J.	Dioxin '89 Proceedings, Toronto, Ontario, September 1989.	This paper summarizes the distribution of concentrations of 2378 substituted dibenzo-p-dioxins and dibenzofurans in bleached kraft and sulfite mill pulps, wastewater sludges, and treated effluents in the U.S. in mid-1988.
127.	Dechlorination and Decolorization of High-Molecular-Weight Chlorolignin from Bleach Plant Effluents by an Oxidation Process	Sun, Y.-B.; Joyce, W.; Chang, H.-M.	TAPPI Journal, September 1989, pp. 209-213.	The total organic chlorine and color of the high-molecular-weight chlorolignin from spent alkali extraction-stage effluent were effectively removed by an oxygen oxidation process. Under the best conditions, about 70-80% of the TOCl and 60-70% of the color were removed in less than one hour. A process combining ultrafiltration, oxidation, and biological treatment could be an effective, economical option to remove TOCl and color from spent alkali extraction effluent.
128.	Treating Bleaching Effluent for Suspended Solids and Color	Garcia-Heras, J.L.; Forster, C.F.	TAPPI Journal, September 1989, pp. 199-206.	The paper discusses a study of the main characteristics of a coagulation system to remove chromophoric compounds from a bleach plant wastewater by iron and calcium cations. The treatment was successful, with a color removal of 99% with an iron dose of 6-7 moles/m3, the residual suspended solids were low (about 10 mg/l), but the residual turbidity (5-10 NTU) was higher than the initial value, and the sludge volume was high (over 20%).
129.	Chlorinated Organic Matter in Bleached Chemical Pulp Production Part IV: The Occurrence of Chlorinated Organic Matter in Bleached Pulp	Reeve, D.W.; Weishar, K.M.	Presented at the CPPA Technical Section Western Conference, Whistler, B.C., May 25-27, 1989.	Some of the chlorine covalently bonded to pulp during chlorination is not removed by hydrolysis or dissolution but remains in the pulp. Total organically-bound chlorine in fully bleached hardwood pulp was found to be in the range 200 to 2200 ug Cl/g oven dry pulp while Cl in fully bleached softwood pulp was not as variable, with the average being approximately 400 ug/g o.d. pulp. Water-extracted AOX was less than 6% of the total.
130.	Monox-L for Decreasing AOX and/or Dioxin	Hurst, M.M.	CPPA Proceedings, 76th Annual Meeting Technical Section, Montreal, Quebec, February 1-2, 1990, pp. B313-B314.	Monox-L is a cost effective bleaching agent which can significantly reduce the levels of both AOX and dioxins produced as compared to conventional bleaching sequences.
131.	Pulping Processes	Rydholm, S.A.	Interscience, New York, 1965.	
132.	Non-chlorine Bleaching of MCC-Pulp	Dillner, B.; Larsson, L.-O.; Tibbling. P.	TAPPI Proceedings, 1989 Pulping Conference, Seattle, Washington.	The paper discusses how a combination of modified continuous cooking (MCC) and oxygen delignification gives a pulp of sufficiently low kappa number (13) for final bleaching without the use of elementary chlorine. MCC oxygen pulp has been bleached D(EO)DD and D(EOP)DD to 90%+ ISO brightness with retained strength characteristics. The effluent load from the D(EOP)DD sequence is expected to be very low, the measured AOX being only 0.9-1.0 kg/ADMT.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
133.	Impact of High Chlorine Dioxide Substitution for Chlorine on the Oxygen Delignified Pulp at Espanola	Munro, F.C.; Chandrasekaran, S.; Cook, C.R.; Pryke, D.C.	TAPPI Proceedings, 1989 Pulping Conference, Seattle, Washington.	E. B. Eddy at Espanola embarked on a mill trial to increase the ClO2 substitution from 10% to 50% in an effort to eliminate polychlorinated dioxins and furans in the bleached pulp and effluent. OC/DEoHD was the bleaching sequence used. The results indicate that at 50% substitution the polychlorinated dioxins are non-detectable in both pulp and effluent and chlorinated organic compounds measured as AOX have decreased significantly in the bleachery effluent.
134.	Personal communication between D.G. Bodien of EPA and O.B Burns, Jr. of Westvaco Corporation	Westvaco Corporation		Communication contains information related to status of process changes (split chlorine addition/pH adjustment) made at the three Westvaco bleached kraft pulp mill, capital cost associated with these changes, and implementation time to design and construction of these changes.
135.	Monox-L Information and Data	Quantum Technologies, Inc.		Information and data related to the use of Monox-L as a bleaching chemical. Including BOD, COD, Color, TOCl, AOX, chloroform and dioxin effluent data, capital and O & M costs and energy requirements.
136.	Personal communication between D.G. Bodien of EPA and C. Whitaker of James River Corporation	James River Corporation		Communication contains analysis for Dibenzofurans in defoamers used at the James River Camas, Washington mill.
137.	Personal communication between D.G. Bodien of EPA and C. Luhrmann and J.J. Miele of Kamyr, Inc.	Kamyr, Incorporated		Communication contains information related to the costs and implementation time for installation of MCC digestion systems.
138.	USEPA/Paper Industry Cooperative Dioxin Screening Study	USEPA, Office of Water Regulations and Standards	EPA-440/1-88-025, March 1988	
139.	Modified Continuous Cooking	Dillner, B.	Paper presented at Kamyr, Inc. Low Chlorine Bleaching Seminar, Atlanta, 1987-12-08.	Modified continuous cooking implies a con/counter-current process where the alkali concentration is lower than normal at the beginning of the cook and is then raised at the end. MCC pulp has a higher than normal viscosity, lower kappa number, equal or better strength and results in a reduction of the effluent load by 25 to 30%.
140.	Oxygen Delignification	Backlund, A.	Paper presented at Kamyr, Inc. Low Chlorine Bleaching Seminar, Atlanta, 1987-12-08.	Paper presents information relative to oxygen delignification. Installations, costs, environmental effects and discussion of high and medium consistency systems are presented.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
141.	On the Formation of PCDDs and PCDFs in the Bleaching of Pulp	Rappe, C.; Swanson, S.; Glas, B.; Kringstad, K.P.; de Sousa, F.; Johansson, L.; Abe, Z.	Pulp & Paper Canada, 90:8, 1989, pp. 42-47.	This investigation was done to obtain a better understanding of the factors influencing the formation of PCDDs and PCDFs in pulp bleaching. The results indicate that unchlorinated dibenzofuran may be a precursor for PCDFs. The role of unchlorinated dibenzo-p-dioxin as precursor is more doubtful. Condensates may promote the formation of PCDDs and PCDFs. The reason for this is at present unclear.
142.	Organo-chlorine Discharges in Wastewaters from Kraft Mill Bleach Plants	Hall, E.R.; Fraser, J.; Garden, S.; Comacchio, L.-A.	Pulp & Paper Canada, 90:1, 1989, pp. 68-72.	Samples were collected from process streams in four kraft bleach plants with different bleaching sequences. Chemical analytical data were compiled to compare the potential suitability of anaerobic treatment technology for dechlorination of the sewered streams. Organo-chlorine concentrations and discharge rates are summarized for each bleaching sequence and for parallel plants bleaching hardwood and softwood pulps, preceded by oxygen delignification.
143.	Mill Trials of Substantial Substitution of Chlorine Dioxide for Chlorine: Part II	Pryke, D.C.	Pulp & Paper Canada, 90:6, 1989, pp. 93-97.	Recent trials in market softwood kraft pulp mills situated on the B.C. coast and in the southern U.S. have shown that increasing chlorine dioxide substitution from 10 to 30 percent in the chlorination stage decreases bleaching chemical consumption and bleaching cost while maintaining pulp quality. Bleaching chemical savings of C$1.50 to 2.50 per tonne were achieved.
144.	Swedish, Finnish Mills and Suppliers Show U of T Students What's New	Earl, P.F.; Odendahl, S.; Martinez, M.; Tomar, P.; Bratu, C.	Pulp & Paper Canada, 90:9, 1989, pp. 17-20.	Paper presented is a trip report for tour of pulp and paper mills, research centers and universities in Sweden and Finland.
145.	Pulp and Paper Technology, Second Edition	Britt, K.W.	Van Nostrand Reinhold Company, New York, 1970.	Text
146.	New Pressurized Compaction Filter Lowers Operating and Capital Costs	Tait, D.	Pulp & Paper, November 1985, pp.	Pulp washer with compaction baffle and pressurization permits low-level installation, lower power consumption, and greater efficiency.
147.	Ultrafiltration for Removing Color from Bleach Plant Effluent	Lundahl, H.; Mansson, I.	TAPPI Journal, April 1980, p. 97.	Paper discusses ultrafiltration for the removal of color from bleach plant effluents.
148.	Closed Cycle Technology Report	Jain, A.K.	NCASI Report, September 1988.	This report is an assessment of the current state of knowledge of various closed cycle technologies. Technologies included are Rapson-Reeve process, Billerud-Uddeholm and other resin processes, activated carbon adsorption, chemical coagulation, ultrafiltration and reverse osmosis. The report also includes information on the problem encountered with implementing these technologies, and recommends the areas of research that could be pursued under the R & D program.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
149.	Modifying the Bleaching Process to Decrease AOX Formation	Liebergott, N.; van Lierop, B.; Nolin, A.; Faubert, M.; Laflamme, J.	CPPA Proceedings, 76th Annual Meeting Technical Section, Montreal, Quebec, February 1-2, 1990, pp. B229-B238.	This report describes the effects of Eo, Eop and O delignification and of a wide range of chlorine dioxide substitution levels in the chlorination stage on the properties of pulp and bleach effluent. Increasing the chlorine dioxide substitution to 70 % produced less chlorinated phenolic compounds in the bleach effluents. The BOD and COD in the effluent decreased only with very high chlorine dioxide substitution levels.
150.	Mill Trials of Substantial Substitution of Chlorine Dioxide for Chlorine	Pryke, D.C.; Francis, R.C.; Reeve, D.W.	TAPPI Proceedings, 1985 Pulping Conference, pp. 543-551.	Three mill trials have recently been conducted in Canada where ClO2 substitution was raised to the 30-50% range. Total equivalent chlorine and caustic consumption decreased significantly in all three mills resulting in savings of $1.55, $1.94 and $2.36 CDN/ADT. Pulp quality parameters were unchanged: strength, cleanliness and brightness. Bleach plant effluent colour and BOD5 were significantly decreased: Toxicity test results were somewhat erratic but decreased toxicity was indicated.
151.	Personal communications between D. G. Bodien of EPA and A. Axelsson of ABB Automation	ABB Automation		Communications contains information related to the STFI OPTI-Kappa analyzer including capital cost, delivery time and installations list.
152.	RDH Pulping - Better Pulp Properties Through Improved Selectivity	Swift, L.K.	Unpublished, available from author or Beloit Corporation.	The steam savings capability of the new RDH cooking technology has been well documented. New studies are surfacing which are beginning to explain why RDH cooking produces pulp of significantly higher strength characteristics than other processes and further more, why RDH cooking can be extended to extraordinarily low Kappa levels.
153.	Personal communications between D. G. Bodien of EPA and messieurs J. Morrison, P. Sullivan and B. Fagerlund of Beloit Corporation	Beloit Corporation		Information in communications relate to costs and implementation times associated with RDH pulping systems.
154.	Peroxide Delignification of Unbleached Chemical Pulp by Minox Process	Carles, J.E.; Lemoyne, H.; Logan. W.R.	TAPPI Proceedings, 1980 Pulping Conference, Atlanta, GA, pp. 325-332.	Unbleached chemical pulp can be delignified by hydrogen peroxide in an alkaline medium. Laboratory results obtained on bisulfite and kraft pulps are described. Using this process on kraft pulp a reduction by 45% of the bleach plant effluent color has been achieved, together with savings in overall bleaching operation costs.
155.	Personal communication between D. G. Bodien of EPA and T. Mullen of Air Products & Chemicals, Inc.	Air Products & Chemicals, Inc.		Communication relates to pulp mills who have purchased, are presently installing or have installed oxygen delignification systems.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
156.	Closed-Cycle Bleached Kraft Pulp Mill - 1978, The	Reeve, D.W.; Rowlandson, G.; Kramer, J.D.;Rapson, W.H.	TAPPI Journal, August 1979, pp.51-54.	Paper discusses the first 15 months of operation of the world's first installation of the closed-cycle bleached kraft pulp mill. The plant has performed well, concentrating white liquor to recover salt which has been use for ClO2 production. Most bleaching systems are readily incorporated in to the closed-cycle mill filtrate recovery strategy. Black liquor evaporator condensate segregation, stripping and reuse are important aspects of the closed-cycle mill and are described along with chemical, water and energy considerations.
157.	Personal communication between D. G. Bodien of EPA and L.-A. Lindstrom and P. Flickenger of Sunds Defibrator	Sunds Defibrator		Communication deals with information related to installation of oxygen delignification systems.
158.	New Catalyst Improves Polysulfide Liquor Makeup, O2 Delignification	Lightfoot, W.E.	Pulp & Paper, January 1990, pp. 88-93.	Paper deals with polysulfide cooking and its impact on the recovery boiler. Use of polysulfide liquor makeup enables mills with limited recovery boiler capacity to employ oxygen delignification. Costs are provided which show that the ROI for the process is on the order of 6-7 months.
159.	Personal communication between D.G. Bodien of EPA and W.E. Lightfoot of Chiyoda International Corporation	Chiyoda International Corporation		Communication deals with polysulfide cooking, installation time for the process and facilities where system is in operation.
160.	Organochlorine Discharges from a Bleached Kraft Pulp Mill with Oxygen Delignification and Secondary Treatment System	Cook, C.R.	CPPA Proceedings, 1988 Environmental Conference, Vancouver, B.C., October 25-27,1988, p.37.	A seven month study of organochlorine loadings from the E.B. Eddy kraft pulp mill in Espanola was completed in July 1988. The study showed that the mill's secondary treatment system discharges less than 1.5 kg AOX/AD tonne of pulp to the receiving water. The majority of the AOX, BOD and TOC removal in the lagoon occurred during the first 2.5 days of treatment in Cell 1 of the lagoon. Cell 1 also removed all of the acute toxicity from this mill effluent in 2.5 days.
161.	Effluent-Free Bleached Kraft Pulp Mill - Part XIII: The Second Fifteen Years of Development, The	Reeve, D.W.	Pulp & Paper	In the 15 years since conception and the 5 years since mill start-up, there has been great progress in the technology of elimination of pulp mill effluents by recycling. Bleach plant effluent use in the pulping chemical recovery cycle and ultimate destruction in the recovery furnace has been demonstrated in mill operation. Recovery of sodium chloride and its use to regenerate bleaching chemicals has also been practiced and proven. Development is continuing.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
162.	Mill Trials of Substantial Substitution of Chlorine Dioxide for Chlorine - Part III: Medium Consistency	Rempel, W.; Pryke, D.C.; Ouchi, M.D.	Unpublished	A recent trial at a market softwood kraft pulp mill on the west coast of British Columbia with a medium consistency chlorination stage has shown that increasing ClO2 substitution from 5 to 50% decreases bleaching chemical consumption, bleaching cost and improves pulp quality. Discharges of chlorinated organic compounds, including PCDDs and PCDFs, from the pulp mill to the receiving water have been decreased by over 50%. PCDDs and PCDFs in bleached pulp have also been decreased substantially.
163.	USEPA/Paper Industry Cooperative Dioxin Study	USEPA, Office of Water Regulations and Standards	Unpublished	
164.	Personal communication between D. G. Bodien of EPA and K. Uhlin of Mo och Domsjo AB	Mo och Domsjo AB		Communication contains information related to the ultrafiltration of the caustic extraction filtrate at the MoDo Husum mill.
165.	NO2 Treatment of Kraft Pulp Followed by Oxygen Bleaching - Influence of Black Liquor	Samuelson, O.; Ojteg, U.	TAPPI Journal, February 1990, pp. 141-146.	Kraft pulp from softwood containing large amounts of black liquor was delignified by oxygen bleaching following pretreatment with nitrogen dioxide. The alkaline pulp was treated with NO2 for a few minutes at high or medium consistency. After ripening for 180 minutes the pulp was oxygen bleached. A kappa number of 3.5 was obtained even when the pulp contained 43 kg of solids from the black liquor per 1000 kg pulp.
166.	Technologies for Reducing Dioxin in the Manufacture of Bleached Wood Pulp - Background Paper	Office of Technology Assessment, Washington, D. C.	Library of Congress, Catalog Card No. 89-600719.	Discussion of alternative technologies to reduce formation of dioxin in bleached pulp. Oxygen pretreatment for delignification and substituting other chemicals for chlorine are evaluated.
167.	Hydrogen Peroxide in Alkaline Extraction Improves Pulp Quality	Hook, J.; Meuller, L.; Wallin, S.	Nordisk Cellulosa 2, No. 2, March 1985, pp. 47-50.	Several bleach plants are using hydrogen peroxide in the alkaline extraction stage. Advantages and disadvantages of this practice are discussed.
168.	Dioxin	Alkaline Paper Advocate	Alkaline Paper Advocate 2, No. 2, July 1989, pp. 17-18.	Summary of mechanisms and effects of dioxin formation in bleached kraft process is presented. Discussion on European, Canadian and U. S. regulatory issues. List of mills using/planning to use oxygen bleaching is given.
169.	New Pollution Control Phase Means More Than Just Dioxin Prevention	Karl, W.	Pulp & Paper Journal (Canada), 41:9, October 1988, pp. 18-21.	Overview of industry's response to the problems of dioxin in bleaching processes. General review of research in Canada, Sweden, Finland & U.S. on dioxin formation and disposition.
170.	PRENOX - Oxidation of Pulp with Nitrogen Dioxide and Oxygen Prior to Oxygen Delignification Could Reduce Pollution	Brannland, R.; Simonson, O.	Swedish Pulp & Paper Journal No. 2, 1986, pp. 48-50, 53-54.	Findings of pilot plant investigations in a mill in Sweden using PRENOX process is discussed. PRENOX process reduced kappa no. in pulp. BOD, COD and TOCl are reduced with decreasing kappa no. Increased washing and chlorine dioxide substitution further reduced TOCl.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
171.	Reduce TOCl with OxO Process	Lachenal, D.; Muquet, M.	CPPA Annual Meeting Preprints, 75B, Montreal, Que., February 2-3, 1989, pp. 187-192.	Findings of OxO process investigations presented. OxO process consists of oxygen delignification followed by low charge of chlorine followed by oxygen extraction stage. OxO process can be optimized to reduce chlorine requirement. Comparison with chlorine dioxide bleaching processes reported.
172.	Reduced Discharge of TOCl with a Hot (EO) Stage	Sjoblom, K.; Hardmeier, P.	TAPPI Proceedings, 1988 International Pulp Bleaching Conference, Orlando, FL, June 5-9, 1988, pp. 263-270.	Chlorine consumption can be reduced by increased temperature in the EO stage. For a given pulp and bleaching sequence, a TOCl level can be achieved for a minimum total consumption of chlorine dioxide in the hot EO stage. If economics permit, peroxide added to the EO stage at 75 C can substitute for an EO stage at 90 C.
173.	How to Cope with TOCl (Total Organically Bound Chlorine)	Brannland, R.; Fossum G.	TAPPI Proceedings, 1987 Pulping Conference, Washington, D. C., November 1-5, 1987, Book 2 pp. 243-248.	Review of regulatory control for TOCl implemented in Swedish mills presented. Effects of TOCl on bottom living organisms in receiving waters presented briefly. Alternatives for reaching TOCl formation in pulp bleaching such as extended delignification, PRENOX, oxygen delignification, chlorine dioxide substitution presented.
174.	Sulfite Mills Move to Cut TOCl	Ducey, M.K., Technical Editor	Pulp & Paper International, 29:12, December 1987, pp. 54-55.	Discussion of results in retrofitting sulfite mills in West Germany and Wisconsin with first stage bleaching using oxygen, peroxide and NaOH. Reduction in chlorine consumption and effluent TOCl achieved as well as reduced toxicity. Cost justification is also discussed.
175.	Dechlorination and Biological Treatment of Chlorinated Organic Substances	Bottoer, J.; Patzold, J.; Krause, T.H., Schempp, W.	International Symposium on Wood Pulping Chemicals Proceedings, Paris, April 27-30, 1987, Vol. 1, pp. 171-174.	Treatment of bleach plant effluent by dechlorination, UV and biological processes reduced AOX by 60%. Post treatment using aerobic fixed-bed reactor reduced AOX by over 90%.
175.	Mill Experience of Oxygen Delignification	Kiumra, M.	Japan TAPPI Journal, 42:1, January 1988, pp. 52-55.	Oxygen delignification in a mill in Japan reduced Kappa No. by 49%. Chlorine consumption and COD in bleaching process reduced by 30% and 50% respectively.
177.	Pretreatment of Pulps with Chlorine Before Oxygen Delignification	Soteland, N.	Nordic Pulp & Paper Research Journal, October 1988, pp. 124-127.	Slight chlorination of pulp oxygen delignification reduces kappa number significantly at mill in Oslo, Norway. Results in low effluent COD, TOCl and reduced mutagenicity.
178.	Environmentally Friendly (Bleaching) Processes of the Future	Axegard, P.	TAPPI Proceedings, 1989 Bleach Plant Operations Seminar, Charleston, SC, March 5-9, 1989, pp. 195-200.	Overview by STFI on ways of reducing TOCl in bleach plant effluents such as extended delignification, oxygen delignification, chlorine dioxide substitution and oxygen extraction. Discussion on treatment of bleach plant effluent using recycling, membrane filtration and biological processes.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
179.	Bleaching Plants For the 90's	Idner, K.	Swedish Pulp & Paper Journal, No. 1, 1987, pp. 50-52.	Review of alternatives for reducing TOCl in bleach plant effluents to meet regulatory requirements, demands for lower production costs, and improved pulp quality. Operating costs are predicted to be lowered by increased use of process control equipment and fewer bleaching stages.
180.	Aerated Dike Decreases Chlorate-Containing Effluents	Axegard, P.; Germgard, U.	Nordisk Cellulosa 3, 45:10, December 1986, pp 56-57.	A five week aerobic treatment can diminish the environmental effect of chlorate, in chlorine dioxide stage bleachery effluents by 85%. The treatment, developed in Sweden, achieved significant reductions in TOCl.
181.	What's Hot in Pulping? Extended Delignification	Renard, J.J.	American Papermaker, 51:3, March 1988, pp. 50-52.	Modifications implemented at a mill in the digester operations to install extended delignification process is described. Developments in chemical pulping alternatives to the kraft process are briefly discussed.
182.	Extended Delignification and Its Potential for Environmental Improvements	Blomberg, B.; Hartler, N.	Nordic Pulp & Paper Research Journal No. 4, December 1986, pp. 25-29.	Improved selectivity in kraft pulping process is discussed. Most important parameter for controlling selectivity is the lignin concentration in the cooking liquor during final phase of cook. Swedish process discussed, which results in a low concentration of lignin in the liquor, therefore a smaller bleaching chemical requirement.
183.	Effect of Chlorine Dioxide substitution on Bleaching Efficiency and the Formation of Organically-Bound Chlorine (3)	Axegard, P.	TAPPI Proceedings, 1986 Pulping Conference, Toronto, October 26-30, 1986, Book 1, pp. 179-186.	Investigation of two alternatives for decreasing the consumption of chlorine by using more chlorine dioxide in the bleaching sequence. Advantages of replacing the Cl which ClO2 at different stages of the sequence, and ratios of formation of different chlorates with decreased Cl consumption are discussed.
184.	Oxygen Delignification as an Alternative to Biological Treatment: A Case Study	Galloway, L.R.; Schmid, E.; Lebidoff, J.W.	Pulp & Paper Canada, 88:1, 1987, p. T26.	A comparison of oxygen delignification and biological treatment used to reduce the effect of kraft pulp mill effluent on receiving waters is presented here.
185.	In-Plant Process Alternatives for Minimizing Discharges of AOX	Earl, P.F.; Reeve, D.W.	Third Colloquium on Pulp and Paper Mill Effluents, Toronto, Ontario, February 14-15, 1989.	Process alternatives for lowering the lignin content in pulp, better washing techniques and chlorine dioxide substitution during bleaching are discussed.
186.	Chemical Inspection Agency Charges Incorrect Dioxin Accounting	Ekstrom, T.	Nordisk Cellulosa 5, 9:1, February 1988, pp. 15-16.	A summary of ongoing dioxin studies being done on Swedish pulp and paper mill effluents is presented. Comparisons are shown for dioxin levels found in chlorine dioxide stages and chlorine stages. Recent studies show that dioxin levels are just as high in chlorine dioxide stages as in chlorine stages.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
187.	Oxygen in a Bleaching Sequence - An Overview	van Lierop, B.; Liebergott, N.; Teodorescu, G.; Kubes, G.J.	PAPRICAN Miscellaneous Report #57, May 1984	By adding oxygen to the extraction stage, the CE/O kappa number of pulps is lowered and translates into chemical savings in the later bleaching stages. The inclusion of an E/O stage into a sequence without lowering the chemical charges in later stage makes it possible to achieve higher brightness targets or decrease the number of bleaching stages. Installation of an E/O stage in a mill bleach plant is straightforward and the payback has been calculated to be about six months to one year.
188.	Overview of Oxidative Bleaching Processes	Liebergott, N.	PAPRICAN Miscellaneous Reports #7, August 1981.	Literature relating to the use of oxidative chemicals in the delignification and brightening operations of pulp bleaching is reviewed. Experimental data on the use of oxygen, ozone and chlorine dioxide in the chlorination stage and hypochlorite, peroxide and oxygen in the extraction stages are also presented. The use of chlorite, chlorate, peracetic acid, nitrogen dioxide, nitrogen trioxide, nitrosyl chloride, chlorine monoxide, fluorine and oxydifluoride as pulp bleaching agents is also discussed.
189.	Evidence that Oil-Based Additives are an Indirect Source of the TCDD and TCDF Produced in Kraft Bleach Plants	Allen, L.H.; Berry, R.M.; Flemming, B.J.; Luthe, C.E.; Voss, R.H.	PAPRICAN Miscellaneous Reports #147, November 1988	Discussion on oil-based defoamers as potential source of furans and dioxin found in bleached pulp. These defoamers could result in elevated levels of 2378-TCDD and 2378-TCDF and act as carriers of the precursor compounds DBF and DBD.
190.	Personal communication between B. Brummit of E. C. Jordan Company and J. Parkinson	Parkinson, J.		Communication contains information related to costs and implementation time for installation of chlorine dioxide generation equipment.
191.	Personal communication between B. Brummit of E. C. Jordan Company and M. Freeland of CRS Sirrine, Inc.	CRS Sirrine, Inc.		Communication contains information related to costs and implementation time for installation of oxygen delignification systems at Union Camp's Eastover mill.
192.	Brown Stock Showers Reduce Dioxin and More	Reynolds, G.	CPPA Proceedings, 76th Annual Meeting Technical Section, Montreal, Quebec, February 1-2, 1990, pp. A237-A240.	Dioxin generation and soda loss can be reduced through improved brown stock washing. The most economical way to achieve this improved washing is through the proper application of the shower filtrate. This paper will discuss the characteristics of the state-of-the-art shower pipe system, a case history on improved washing through the use of this system, and the effect of shower performance on the reduction of dioxin.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
193.	Effects of Secondary Treatment on AOX Levels in Kraft Mill Effluents, The	Dubelsten, P.; Gray, N.C.C.	CPPA Proceedings, 76th Annual Meeting Technical Section, Montreal, Quebec, February 1-2, 1990, pp. A317-A324.	Curtailing the release of chlorinated bleaching effluent into the environment has become a major challenge for the Canadian pulp and paper industry. It is possible that this may be achieved, in part, with secondary effluent treatment. Aerated lagoons are capable of reducing chlorinated phenolics by 20-60% and AOX by up to one third. Improved removal efficiencies of 75-95% for the chlorinated phenolics and 50-65% for AOX, have been observed with activated sludge treatment.
194.	Hydrogen Peroxide Technology for Chlorine Reduction	Anderson, J.R.; Carmichael, D.L.	CPPA Proceedings, 76th Annual Meeting Technical Section, Montreal, Quebec, February 1-2, 1990, pp. B209-B216.	A technology for chlorine reduction involving the use of hydrogen peroxide in conventional alkaline extraction stages is described. Mills that have used peroxide have achieved chlorine reductions of 20-35% and have shifted operations into a "no detectable dioxin" regime. This use of hydrogen peroxide is emerging as an alternative technology for reduction in chlorine consumption; in addition it has been shown to work in combination with other chlorine reduction technologies to achieve very significant reductions in AOX level.
195.	Implementation in Full Scale - The Next Step for PRENOX®	Brannland, R.; Lindstrom, L.-A.; Norden, S.	Sunds Defibrator	In the PRENOX process, softwood kraft pulp is treated with nitrogen dioxide, NO2, prior to oxygen delignification. This allows for a significant decrease in the kappa number after the oxygen stage. This paper presents results of laboratory and pilot plant trials, Results concerning incineration of nitrogen containing black liquors in full scale is also presented.
196.	Efficient Post Oxygen Washing - Crucial for Low Bleach Plant Emissions	Lindstrom, L.-A.; Norden, S.	To be given at APPITA 1990 Conference, New Zealand, April 1990.	Oxygen delignified pulp with a Kappa No of 17.7 was bleached in a C50/D50EoD sequence. Wash losses, measured as COD, were varied from 0 -20 kg/bdt. At optimum bleaching conditions, the incremental increase of active chlorine due to increased carry-over was estimated at 0.5-0.6 kg act. Cl/bdt. AOX discharge increased about 40% at 20 kg COD/bdt compared with completely washed pulp. The sum of tri- and tetrachlorophenolic compounds formed during bleaching, was roughly doubled at a high wash loss compared with completely washed pulp.
197.	Oxygen Delignification - Influence of Kappa Number After Cooking and Degree of Delignification in the Oxygen Stage on Yield, Bleachability and Pulp Quality	Lindstrom, L.-A.	Paper presented at in INSKO Meeting, Helsingfors, Finland, October 12, 1989.	Oxygen delignification is playing an important role in the transformation to bleaching systems without molecular chlorine and will do so even more pronounced in the future. Oxygen delignification, combined with modified kraft cooking or other emerging technologies, will make it possible to reach very low kappa number levels prior to bleaching, and thus meet far-reaching environmental demands on the pulp and paper industry.
198.	Plant Start-up of Monox-L Generator in Kuusankoski, Finland	Yant, R.; Smeds, U.; Hassi, H.	CPPA Proceedings, 76th Annual Meeting Technical Section, Montreal, Quebec, February 1-2, 1990, pp. B315-B319.	Recent environmental concerns and requirements have increased pressure on the pulp bleaching industry to reduce TOCls, dioxins, and chloroform in the bleaching process. The problem arises when pulp mills try to maintain a high-quality pulp and at the same time, keep capital and operating costs at a minimum. Quantum has developed the Monox-L chemical process to meet these demands. This paper discusses the start-up of a Monox-L facility in Kuusankoski, Finland.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
199.	Methods to Minimize the Formation of Lipofilic Chloroorganics in Bleaching	Axegard, P.	TAPPI Proceedings, 1988 Pulping Conference, New Orleans, LA, pp. 307-314.	Conventional, oxygen delignified and PRENOX treated softwood kraft pulps have been bleached in the laboratory. The consumption of Cl2 and the ClO2 substitution level were varied over a large range. AOX is reduced linearly with a decreased consumption of the elemental chlorine in molecular Cl2 and ClO2. Chlorinated phenolics were found to be affected strongly by the Cl2 consumption. Below a Cl2 multiple of about 0.05 virtually no highly chlorinated phenolics could be found.
200.	Personal communication between B. Brummit of E. C. Jordan Company and R. Sherwood of Pope & Talbot Inc.	Pope & Talbot Inc.		Communication contains information related to capital costs and chemical cost savings associated with oxygen extraction.
201.	Unpublished data collected as part of Pulp, Paper and Paperboard Point Source Category Effluent Limitations Guidelines Revision	USEPA, Office of Water Regulations and Standards	Unpublished data	Unpublished data collected as part of Pulp, Paper and Paperboard Point Source Category Effluent Limitations Guidelines Revision.
202.	EO X EO Prebleaching: A Way to Reduce the Formation of AOX	Lachenal, D.; Muguet, M.; Joly, P.	TAPPI Proceedings, 1990 Environmental Conference, Seattle, Washington, April 9-11, 1990, pp. 265-269.	Various pulps (bisulphite and kraft) were prebleached by EO x EO in which x was a low multiple chlorination with partial substitution of ClO2 for Cl2 and EO an oxygen treatment carried out in conditions similar to those in a conventional oxygen reinforced extraction. Thirty percent delignification or more was achieved after the first EO stage and full bleaching was easily obtained by adding H or D or DED treatments. AOX formation was lower than 2 kg per ton of pulp.
203.	On-Site Evaluation of a Teflon-Based Ultraviolet Light System and Hydrogen Peroxide for the Degradation of Color and Chlorinated Organics in Pine Eo from Kraft Mill Bleach Plant Effluents	Smith, J.E., II; Frailey, M.M.	TAPPI Proceedings, 1990 Environmental Conference, Seattle, Washington, April 9-11, 1990, pp. 101-110.	Data collected from laboratory and field investigations showed that the UV hydrogen peroxide process could successfully and economically remove color from Pine Eo filtrate. The reaction were found to be dependent on both the intensity of UV applied to the system as well as on the concentration of hydrogen peroxide used. An overall 80% reduction in apparent color and 85% reduction in AOX was achieved at operating cost competitive with other technologies. The process did not produce a sludge.
204.	Environmental Aspects of Short-Sequence Bleaching	Suss, H.U.; Eul, W.L.; Nimmerfroh, N.; Meier, J.	TAPPI Proceedings, 1990 Environmental Conference, Seattle, Washington, April 9-11, 1990, pp. 503-513.	Low kappa factor chlorination, recommended to decrease the amount of halogenated compounds in the effluent, results in insufficient delignification. The results of studies show that the application of oxygen delignification is more effective in reducing halogenated compounds than chlorine dioxide substitution. Very low levels of halogenated compounds are the result of high-intensity oxygen delignification followed by chlorine dioxide and hydrogen peroxide treatment.

	TITLE	AUTHOR	REFERENCE	SYNOPSIS
205.	AOX Reduction in Bleach Plant Effluent Using Enhanced Oxidation	Smith, P.W.	TAPPI Proceedings, 1990 Environmental Conference, Seattle, Washington, April 9-11, 1990, pp. 769-772.	The use of second generation enhanced oxidation processing (EOP) designed to reduce chlorinated phenolics (AOX) in bleach plant effluent was studied. Mill trials were conducted in order to optimize treatment alternatives under varying production conditions. Appropriate amount of high intensity ultraviolet light together with chemical oxidants (ozone and H2O2) were applied to reliably reduce influent AOX levels from 3.5-4.0 kg/tonne to 2.5 and 1.5 kg/tonne.
206.	Hydrogen Peroxide Addition to Eo Bleaching Stages is Beneficial	Althouse, B.B.	Pulp & Paper, June 1988, pp. 68-70.	The addition of both peroxide and oxygen in the first extraction stage will allow improved production at very low capital costs. Benefits include a decrease in the E stage kappa of 10-25% with an increase in brightness of 5-15 points.